Bretherick's
Handbook of
Reactive Chemical Hazards
Sixth Edition

Volume 2

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AN INDEXED GUIDE TO PUBLISHED DATA

Bretherick's Handbook of **Reactive Chemical Hazards**

Sixth Edition — Volume 2

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Introduction

**THIS SHOULD BE READ THROUGH CAREFULLY
TO GAIN FULL BENEFIT FROM WHAT FOLLOWS**

Aims of the Handbook

This compilation has been prepared and revised to give access to a wide and up-to-date selection of documented information to research students, practising chemists, safety officers and others concerned with the safe handling and use of reactive chemicals. This will allow ready assessment of the likely potential for reaction hazards which may be associated with an existing or proposed chemical compound or reaction system.

A secondary, longer-term purpose is to present the information in away which will, as far as possible, bring out the causes of, and interrelationships between, apparently disconnected facts and incidents. This is designed to encourage an increased awareness of potential chemical reactivity hazards in school, college and university teaching laboratories, and to help to dispel the relative ignorance of such matters which is still in evidence in this important area of safety training during the formative years of technical education.

Others involved in a more general way with the storage, handling, packing, transport and distribution of chemicals, or emergencies related thereto, are likely to find information of relevance to their activities.

Scope and source coverage

This Handbook includes all information which had become available to the editor by January 1999 on the reactivity hazards of individual elements or compounds, either alone or in combination. Appropriate source references are included to give access to more expansive information than that compressed into the necessarily abbreviated text entries.

A wide variety of possible sources of published information has been scanned to ensure maximum coverage. Primary sources have largely been restricted to journals known to favour or specialise in publication of safety matters, and the textbook series specialising in synthetic and preparative procedures.

Secondary sources have been a fairly wide variety of both specialised and general textbooks and encyclopaedic collections (notably those of Mellor, Sidgwick, Pascal and Bailar in the inorganic area, Houben-Weyl in the organic and

organometallic areas, and Kirk-Othmer in the industrial area). Section 50 of *Chemical Abstracts*, the CAS selection *Chemical Hazards, Health, & Safety*, the *Universities' Safety Association Safety News*, the CIA CISHC *Chemical Safety Summary*, (publication of which ceased in 1986 after 56 years), and the IChE *Loss Prevention Bulletin* have been rich sources, together with the more recent RSC *Laboratory HazardsBulletin* and *Chemical Hazards in Industry*. Additionally, various safety manuals, compilations, summaries, data sheets and case histories have been used, and fuller details of all the sources used are set out in Appendix 1. References in the text to textbooks are characterised by absence of the author's initials after the surname.

More recently, some reports have been picked from the Internet, when two of the three following conditions obtained: the editor finds the report credible; it represents a hazard not already present in the handbook; or the source is authoritative. Information on toxic hazards has been specifically excluded because it is available elsewhere in many well-ordered and readily usable forms.

However, it should be remembered that many of the compounds included in this Handbook show high reactivity of one sort or another toward other materials, so may in general terms be expected to be reactive even in brief contact with animal organisms or tissue (including yours), with possible toxic effects, either acute or chronic. Also, no attempt has been made to include details of all flammable or combustible materials capable of burning explosively when mixed with air and ignited, nor of any incidents related to this most frequent cause of accidents, such information again being available elsewhere.

However, to focus attention on the potential hazards always associated with the use of flammable and especially highly flammable substances, some 560 gases and liquids with flash points below 25˚C and/or autoignition temperature below 225˚C have been included in the text, their names prefixed with a dagger. The numerical values of the fire hazard-related properties of flashpoint, autoignition temperature and explosive (flammability) limits in air where known are given in the Five Data Table. Those elements or compounds which ignite on exposure to air are included in the text, but not in the Table.

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General arrangement

The information presented on reactive hazards is of two main types, specific or general, and these types of information have been arranged differently in their respective separate volumes 1 and 2.

FOR CROSS REFERENCES IN CAPITALS, PAGE NUMBERS REFER TO VOLUME 2.

Specific information on instability of individual chemical compounds, and on hazardous interactions of elements and/or compounds, is contained in the main formula-based Volume 1 of the Handbook. For an example of an unstable compound,

see Ethyl perchlorate

For an example of a hazardous interaction between 2 compounds,

see Nitric acid: Acetone

or 2 separate examples involving the same compound,

see Nitric acid: Acetone, or: Ethanol
and one involving 3 compounds,
see Hydrogen peroxide: Nitric acid, Thiourea

General information relating to classes or groups of elements or compounds possessing similar structural or hazardous characteristics is contained in the smaller alphabetically based Volume 2.

See ACYL NITRATES
PYROPHORIC METALS

References in the text to these general classes or groups of materials is always in small capitals to differentiate them from references to specific chemicals, the names of which are given in normal roman typeface.

Some individual materials of variable composition (substances) and materials which cannot conveniently be formulated and placed in Volume 1 are also included in this general section.

See BLEACHING POWDER, CELLULOSE NITRATE

Both theoretical and practical hazard topics, some indirectly related to the main theme of this book, are also included.

See DISPOSAL, EXPLOSIBILITY
GAS CYLINDERS, OXYGEN ENRICHMENT

Several topics which bring together incidents involving a common physical cause or effect but different types of chemicals are now included in Volume 2.

See CATALYTIC IMPURITY INCIDENTS
GAS EVOLUTION INCIDENTS

Specific chemical entries (Volume 1)

A single unstable compound of known composition is placed in the main first volume and is located on the basis of its empirical molecular formula expressed in the Hill system used by *Chemical Abstracts* (C and H if present, then all other element symbols alphabetically). The use of this indexing basis permits a compound to be located if its structure can be drawn, irrespective of whether a valid name is known for it. A representation of the structure of each compound is given on the third bold title line while the name of the compound appears as the first bold title line. References to the information source are given, followed by a statement of the observed hazard, with any relevant explanation. Cross-reference to similar compounds, often in a group entry, completes the entry. *See* Trifluoroacetyl nitrite.

Where two or more elements or compounds are involved in a reactive hazard, and an intermediate or product of reaction is identifiable as being responsible for the hazard, both reacting substances are normally cross-referred to the identified product. The well-known reaction of ammonia and iodine to give explosive nitrogentriodide-ammonia is an example of this type. The two entries

Ammonia: Halogens
Iodine: Ammonia

are referred back to the main entry under the identified material

Nitrogen triodide-ammonia

No attempt has been made, however, to list all combinations of reactants which can lead to the formation of a particular main entry compound.

In a multi-reactant system where no identification of an unstable product was possible, one of the reactants had to be selected as primary reactant to prepare and index the main entry, with the other material(s) as secondary reactant(s). No strictly logical basis of choice for this is obvious.

However, it emerged during the compilation phase that most two component reaction hazard systems of this type involve a fairly obvious oxidant material as one of the reactants. Where this situation was recognised, the oxidant has normally been selected as primary (indexing) reactant, with the other as secondary reactant, following the colon.

See Potassium permanganate: Acetic acid, etc.

In the markedly fewer cases where an obvious reducant has been involved as one reactant, that was normally selected as primary reactant.

See Lithium tetrahydroaluminate: 3,5-Dibromocyclopentene

In the relatively few cases where neither (or none) of the reactants can be recognised as an oxidant or reducant, the choice was made which appeared to give the more informative main entry text.

See Chloroform: Acetone, etc.

Where some hazard has been noted during the preparation of a specific compound, but without it being possible to identify a specific cause, an entry for that compound states 'Preparative hazard', and back-refers to the reactants involved in the preparation.

See Sulfur dioxide

Occasionally, departures from these considerations have been made where such action appeared advantageous in bringing out a relationship between formally unrelated compounds or hazards. In all multi-component cases, however, the secondary reactants (except air and water) appear as formula entries back-referred to the main entry text, so that the latter is accessible from either primary or secondary reactants.

See Dimethyl sulfoxide: Acyl halides (main entry)

Acetyl chloride: Dimethyl sulfoxide (back reference)

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Grouping of Reactants

There are advantages to be gained in grouping together elements or compounds showing similar structure or reactivity, because this tends to bring out the relationships between structure and activity more clearly than separate treatment. This course has been adopted widely for primary reactants (see next heading), and for secondary reactants where one primary reactant has been involved separately with a large number of secondary materials. Where possible, the latter have been collected together under a suitable general group title indicative of the composition or characteristics of those materials.

See Chlorine: Hydrocarbons

Hydrogen peroxide: Metals, Metal oxides, Metal salts

Hydrogen sulfide: Oxidants

This arrangement means, however, that some practice will be necessary on the user's part in deciding into what group an individual secondary reactant falls before the longer-term advantages of the groupings become apparent. The formal group titles listed in Volume 2, Appendix 3, and classified in Appendix 4, will be of use in this connection. However, it should be noted that sometimes informal group titles are used which do not appear in these Appendices.

General group entries (Volume 2)

In some cases literature references relating to well-defined groups of hazardous compounds or to hazard topics have been found, and these are given, with a condensed version of relevant information at the beginning of the topic or group entry, under a suitable bold title, the latter being arranged in alphabetical order in Volume 2.

Cross references to related group or sub-group entries are also included, with a group list of the names and serial (not page) numbers of the chemicals appearing in Volume 1 which lie within the structural or functional scope of the group entry title. Compounds which are closely similar to, but not in strict conformity with, the group definition are indicated by a prefixed asterisk.

The group entries thus serve as sub-indexes for each structurally based group of hazardous compounds. Conversely, each individual compound entry is back-referred to the group entry, and thence to all its strict structural analogues and related congeners included in Volume 1 of this Handbook. Note that these group lists of chemicals are now in alphabetical (not formula) order, and give the serial-number (not page number) for the chemical.

These features should be useful in attempts to estimate the stability or reactivity of a compound or reaction system which does not appear in this Handbook. The effects on stability or reactivity of changes in the molecular structure to which the destabilising or reactive group(s) is attached are in some cases discussed in the group entry. Otherwise such information may be gained from comparison of the information available from the individual compound entries listed collectively (now in alphabetical order, with serial number) in the group entry.

Care is, however, necessary in extrapolating from the described properties of compounds to others in which the user of this Handbook may be interested. Due allowance must be made for changes in elemental reactivity up or down the columns of the Periodic Table, and for the effects of variation in chain length, branching and point of group-attachment in organic systems. Purity of materials, possible catalytic effects (positive or negative) of impurities, and scale of operations may all have a direct bearing upon a particular reaction rate. These and other related matters are dealt with in more detail in the following Introductory Chapter.

Nomenclature

With the direct encouragement and assistance of the Publishers, an attempt has been made to use chemical names which conform to recent recommendations of IUPAC. While this has not been an essential part of the compilation, because

each title name has the corresponding structural and molecular formula adjacent, it seems none the less desirable to minimise possible confusion by adopting the unambiguous system of nomenclature presented in the IUPAC publications.

Where the IUPAC name for a compound is very different from a previously used recent trivial name, the latter is included as a synonym in parentheses (and in single quotes where no longer an acceptable name). Generally, retained trivial names have not been used as main entry titles, but they have been used occasionally in the entry texts. Rarely, on the grounds of brevity, names not conforming strictly to IUPAC principles but recommended for chemicals used in industry in BS 2474: 1983 have been used. The prefix mixo-,to represent the mixtures of isomers sometimes used as industrial materials, is a case in point.

Some of the rigidly systematic names selected by the Association for Science Education for their nomenclature list in 1985 from the IUPAC possibilities, and some of the systematic indexing names used by *Chemical Abstracts* since 1972, are given as synonyms in the Index of Chemical Names (Appendix 4). This should assist those coming into industry and research with a command of those nomenclature systems but who may be unfamiliar with the current variety of names used for chemicals. The inclusion where possible of the CAS Registry Number for each title compound should now simplify the clarification of any chemical name or synonym problems, by reference to the Registry Handbook or other CAS source.

In connection with the group titles adopted for the alphabetically ordered Volume 2, it has been necessary in some cases to devise groupnames (particularly in the inorganic field) to indicate in a very general way the chemical structures involved in various classes, groups or sub-groups of compounds.

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For this purpose, all elements have been considered either as METALS or NON-METALS, and of the latter, HALOGENS, HYDROGEN, NITROGEN, OXYGEN, and SULFUR were selected as specially important. Group names have then been coined from suitable combinations of these, such as the simple

METAL OXIDES, NON-METAL SULFIDES,
N-HALOGEN COMPOUNDS, NON-METAL HYBRIDES,
METAL NON-METALLIDES, COMPLEX HYBRIDES

or the more complex

METAL OXOHALOGENATES
AMMINECHROMIUM PEROXOCOMPLEXES
OXOSALTS OF NITROGENOUS BASES
METALOXONON-METALLATES

Organic group entries are fairly conventional, such as

HALOALKENES
NITROARL COMPOUNDS
DIAZONIUM SALTS

Where necessary, such group names are explained in the appropriate group entry, of which a full listing is given in Volume 2, Appendix 3, and a classified listing in Appendix 4.

Cross reference system

The cross-reference system adopted in this Handbook plays a large part in providing maximum access to, and use of, the rather heterogeneous collection of information herein. The significance of the five types of cross-reference which have been used is as follows.
See... refers to a directly related item.
See also... refers to an indirectly related item.
See other... refers to listed strict analogues of the compound etc.
See related... refers to listed related compounds(congeners) or groups not strictly analogous structurally.
See entry... points to a, or the relevant, reference in Volume 2.

Information content of individual entries

A conscious effort has been made throughout this compilation to exclude all fringe information not directly relevant to the involvement of chemical reactivity in the various incidents o observations, with just enough detail present to allow the reader to judge the relevance or otherwise of the quoted reference(s) to his or her particular reactivity problems or interests.

It must be stressed that this book can do no more than to serve as a guide to much more detailed information available via the quoted references. It cannot relieve the student, the chemist and their supervisors of their moral and now legal obligation to themselves and to their co-workers, to equip themselves with the fullest possible information from the technical literature resources which are widely available, *before* attempting any experimental work with materials known, or suspected, to be hazardous or potentially so. It could be impossible for you *after* the event.

THE ABSENCE OF A MATERIAL OR A COMBINATION OF MATERIALS FROM THIS HANDBOOK CANNOT BE TAKEN TO IMPLY THAT NO HAZARD EXISTS. LOOK THENFOR ANALOGOUS MATERIALS USING THE GROUP ENTRY SYSTEM AND THE INDEXES THERETO.

One aspect which, although it is excluded from most entry texts, is nevertheless of vital importance, is that of the potential for damage, injury or death associated with the various materials and reaction systems dealt with in this Handbook.

Though some of the incidents have involved little or no damage (*see* CAN OF BEANS), others have involved personal injuries, often of unexpected severity (*See* SODIUM PRESS), and material damage is often immense. For example, the incident given under Perchloric acid: Cellulose derivatives,(reference 1) involved damage to 116 buildings and a loss approaching $ 3M at 1947 values. The death-toll associated with reactive chemical hazards has ranged from 1 or 2 (see Tetrafluoroethylene: Iodine pentafluoride) to some 600 with 2000 injured in the incident at Oppau in 1921 (*see* Ammonium nitrate, reference 4), and now to several thousand

with more than 100,000 injured by methyl isocyanate fumes at Bhopal in 1984 (reference 7).

This sometimes vast potential for destruction again emphasises the need to gain the maximum of detailed knowledge *before* starting to use an unfamiliar chemical or reaction system.

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Reactive Chemical Hazards

CROSS REFERENCES IN CAPITALS REFER TO PAGE NUMBERS IN VOLUME 2.

This introductory chapter seeks to present an overview of the complex subject of reactive chemical hazards, drawing attention to the underlying principles and to some practical aspects of minimising such hazards. It also serves in some measure to correlate some of the topic entries in the alphabetically arranged Volume 2 of the Handbook.

Basics

All chemical reactions implicitly involve energy changes (energy of activation + energy of reaction), for these are the driving force. The majority of reactions liberate energy as heat (occasionally as light or sound) and are termed exothermic. In a minority of reactions, energy is absorbed into the products, when both the reaction and its products are described as endothermic.

All reactive hazards involve the release of energy in quantities or at rates too high to be absorbed by the immediate environment of the reacting system, and material damage results. The source of the energy may be an exothermic multi-component reaction, or the exothermic decomposition of a single unstable (often endothermic) compound.

All measures to minimise the possibility of occurrence of reactive chemical hazards are therefore directed at controlling the extent and rate of release of energy in a reacting system. In an industrial context, such measures are central to modern chemical engineering practice. Some of the factors which contribute to the possibility of excessive energy release, and appropriate means for their control, are now outlined briefly, with references to examples in the text.

Kinetic Factors

The rate of an exothermic chemical reaction determines the rate of energy release. so factors which affect reaction kinetics are important in relation to possible reaction hazards. The effects of proportions and concentrations of reactants upon reaction rate are governed by the Law of Mass Action, and there are many examples where changes in proportion and/or concentration of reagents have transformed an

established uneventful procedure into a violent incident. For examples of the effect of increase in proportion,

see 2-Chloronitrobenzene: Ammonia
Sodium 4-nitrophenoxide

For the effect of increase in concentration upon reaction velocity,

see Dimethyl sulfate: Ammonia
Nitrobenzene: Alkali (reference 2)

The effects of catalysts (which effectively reduce the energy of activation), either intentional or unsuspected, is also relevant in this context. Increase in the concentration of a catalyst (normally used at 1–2%) may have a dramatic effect on reaction velocity.

See Trifluoromethanesulfonic acid: Acyl chlorides, etc.
2-Nitroanisole: Hydrogen
HYDROGEN CATALYSTS

The presence of an unsuspected contaminant or catalytic impurity may affect the velocity or change the course of reaction. For several examples,

See CATALYTIC IMPURITY INCIDENTS

In the same context, but in opposite sense, the presence of inhibitors (negative catalysts, increasing energy of activation) may seriously interfere with the smooth progress of a reaction. An inhibitor may initiate an induction period which can lead to problems in establishing and controlling a desired reaction. For further details and examples,

See INDUCTION PERIOD INCIDENTS

Undoubtedly the most important factor affecting reaction rates is that of temperature. It follows from the Arrhenius equation that the rate of reaction will increase exponentially with temperature. Practically, it is found that an increase of 10°C in reaction temperature often doubles or trebles the reaction velocity.

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Because most reactions are exothermic, they will tend to accelerate as reaction proceeds unless the available cooling capacity is sufficient to prevent rise in temperature. Note that the exponential temperature effect accelerating the reaction will exceed the (usually) linear effect of falling reactant concentration in decelerating the reaction. When the exotherm is large and cooling capacity is inadequate, the resulting accelerating reaction may proceed to the point of loss of control (runaway), and decomposition, fire or explosion may ensue.

The great majority of incidents described in the text may be attributed to this primary cause of thermal runaway reactions. The scale of the damage produced is related directly to the size, and more particularly to the rate, of energy release.

See RUNAWAY REACTIONS

Reactions at high pressure may be exceptionally hazardous owing to the enhanced kinetic energy content of the system.

See HIGH-PRESSURE REACTION TECHNIQUES

Although detailed consideration of explosions is outside the scope of this Handbook, three levels of intensity of explosion (i.e. rates of fast energy release) can be discerned and roughly equated to the material damage potential.

Deflagration involves combustion of a material, usually in presence of air. In a normal liquid pool fire, combustion in an open situation will normally proceed

without explosion. Mixtures of gases or vapours with air within the explosive limits which are subsequently ignited will burn at normal flame velocity (a few m/s) to produce a 'soft' explosion, with minor material damage, often limited to scorching by the moving flame front. Injuries to personnel may well be more severe.

If the mixture (or a dust cloud) is confined, even if only by surface irregularities or local partial obstructions, significant pressure effects can occur. Fuel-air mixtures near to stoicheiometric composition and closely confined will develop pressures of several bar within milliseconds, and material damage will be severe. Unconfined vapour explosions of large dimensions may involve higher flame velocities and significant pressure effects, as shown in the Flixborough disaster.

See DUST EXPLOSION INCIDENTS
PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION
VAPOUR CLOUD EXPLOSIONS

Detonation is an extreme form of explosion where the propagation velocity becomes supersonic in gaseous, liquid or solid states. The temperatures and particularly pressures associated with detonation are higher by orders of magnitude than in deflagration. Energy release occurs in a few microseconds and the resulting shattering effects are characteristic of detonation. Deflagration may accelerate to detonation if the burning material and geometry of confinement are appropriate (endothermic compounds, long narrow vessels or pipelines).

See Acetylene (reference 9)
ENDOTHERMIC COMPOUNDS
EXPLOSIONS
UNIT PROCESS INCIDENTS

Factors of importance in preventing such thermal runaway reactions are mainly related to the control of reaction velocity and temperature within suitable limits. These may involve such considerations as adequate heating and particularly cooling capacity in both liquid and vapour phases of a reaction system; proportions of reactants and rates of addition (allowing for an induction period); use of solvents as diluents and to reduce viscosity of the reaction medium; adequate agitation and mixing in the reactor; control of reaction or distillation pressure; use of an inert atmosphere.

See AGITATION INCIDENTS

In some cases it is important not to overcool a reaction system, so that the energy of activation is maintained.

See Acetylene: Halogens (reference 1)

Adiabatic Systems

Because process heating is expensive, lagging is invariably applied to heated process vessels to minimise heat loss, particularly during long-term hot storage. Such adiabatic or near-adiabatic systems are potentially hazardous if materials of limited thermal stability, or which possess self-heating capability, are used in them. Insufficiently stabilised bulk-stored monomers come into the latter category.

See 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, Solvent
POLYMERISATION INCIDENTS

SELF-HEATING AND IGNITION INCIDENTS
THERMAL STABILITY OF REACTION MIXTURES
VIOLENT POLYMERISATION

Reactivity vs. Composition and Structure

The ability to predict reactivity and stability of chemical compounds from their composition and structure is as yet limited, so the ability accurately to foresee potential hazards during preparation, handling and processing of chemicals and their mixtures is also restricted. Although some considerable progress has been made in the use of computer programs to predict hazards, the best available approach for many practical purposes appears to be an initial appraisal based on analogy with, or extrapolation from, data for existing compounds and processes. This preliminary assessment should be supplemented with calorimetric instrumental examination, then bench-scale testing procedures for thermal stability applied to realistic reaction mixtures and processing conditions. A wide range of equipment and techniques is now available for this purpose.

See ACCELERATING RATE CALORIMETRY
ASSESSMENT OF REACTIVE CHEMICAL HAZARDS
COMPUTATION OF REACTIVE CHEMICAL HAZARDS
DIFFERENTIAL SCANNING CALORIMETRY
DIFFERENTIAL THERMAL ANALYSIS
MAXIMUM REACTION HEAT
REACTION SAFETY CALORIMETRY

It has long been recognised that instability in single compounds, or high reactivity in combinations of different materials, is often associated with particular groupings of atoms or other features of molecular structure, such as high proportions or local concentrations of oxygen or nitrogen. Full details of such features associated with explosive instability are collected under the heading EXPLOSIBILITY.

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An approximate indication of likely instability in a compound may be gained from inspection of the empirical molecular formula to establish stoicheiometry.

See HIGH-NITROGEN COMPOUNDS
OXYGEN BALANCE

Endothermic compounds, formed as the energy-rich products of endothermic reactions, are thermodynamically unstable and may be liable to energetic decomposition with low energy of activation.

See ENDOTHERMIC COMPOUNDS

Reaction Mixtures

So far as reactivity between different compounds is concerned, some subdivision can be made on the basis of the chemical types involved. Oxidants (electron sinks) are undoubtedly the most common chemical type to be involved in hazardous incidents, the other components functioning as fuels or other electron sources. Air (21% oxygen) is the most widely dispersed oxidant, and air-reactivity may lead to either short- or long-term hazards.

Where reactivity of a compound is very high, oxidation may proceed so fast in air that ignition occurs.

See PYROPHORIC MATERIALS

Slow reaction with air may lead to the longer-term hazard of peroxide formation.

See AUTOXIDATION
PEROXIDATION INCIDENTS
PEROXIDATION IN SOLVENTS
PEROXIDISABLE COMPOUNDS

Oxidants more concentrated than air are of greater hazard potxential, and the extent of involvement of the common oxidants

Perchloric acid
Chlorine
Nitric acid
Hydrogen peroxide
Sulfuric acid

METAL CHLORATES

may be judged from the large number of incidents in the text involving each of them, as well as other OXIDENTS.

At the practical level, experimental oxidation reactions should be conducted to maintain in the reacting system a minimum oxygen balance consistent with other processing requirements. This may involve adding the oxidant slowly with appropriate mixing and cooling to the other reaction materials to maintain the minimum effective concentration of oxidant for the particular reaction. It will be essential to determine by a suitable diagnostic procedure that the desired reaction has become established, to prevent build-up of unused oxidant and a possible approach to the oxygen balance point.

See OXYGEN BALANCE

Reducants (rich electron sources) in conjunction with reducible materials (electron acceptors) feature rather less frequently than oxidants in hazardous incidents.

See REDUCANTS

Interaction of potent oxidants and reducants is invariably highly energetic and of high hazard potential.

See Dibenzoyl peroxide: Lithium tetrahydroaluminate
Hydrazine: Oxidants

REDOX REACTIONS
ROCKET PROPELLANTS

Similar considerations apply to those compounds which contain both oxidising and reducing functions in the same molecular structure.

See REDOX COMPOUNDS

Water is, after air, one of the most common reagents likely to come into contact with reactive materials, and several classes of compounds will react violently, particularly with restricted amounts of water.

See WATER-REACTIVE COMPOUNDS

Most of the above has been written with deliberate processing conditions in mind, but it must be remembered that the same considerations will apply, and

perhaps to a greater degree, under the uncontrolled reaction conditions prevailing when accidental contact of reactive chemicals occurs in storage or transit.

Adequate planning is therefore necessary in storage arrangements to segregate oxidants from fuels and reducants, and fuels and combustible materials from compressed gases and water-reactive compounds. This will minimise the possibility of accidental contact and violent reaction arising from faulty containers or handling operations, and will prevent intractable problems in the event of fire in the storage areas.

See SAFE STORAGE OF CHEMICALS

Unexpected sources of ignition may lead to ignition of flammable materials during chemical processing or handling operations.

See FRICTIONAL IGNITION OF GASES
IGNITION SOURCES
SELF-HEATING AND IGNITION INCIDENTS
STATIC INITIATION INCIDENTS

Protective Measures

The need to provide protective measures will be directly related to the level of potential hazards which may be assessed from the procedures outlined above. Measures concerned with reaction control are frequently mentioned in the following text, but details of techniques and equipment for personal protection, though usually excluded from the scope of this work, are obviously of great importance.

Careful attention to such detail is necessary as a second line of defence against the effects of reactive hazards. The level of protection considered necessary may range from the essential and absolute minimum of effective eye protection, via the safety screen, fume cupboard or enclosed reactor, up to the ultimate of a remotely controlled and blast-resistant isolation cell (usually for high-pressure operations). In the absence of facilities appropriate to the assessed level of hazard, operations must be deferred until such facilities are available.

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Volume 2

Class, Group and Topic

(Entries arranged in alphabetical order)

EXPLANATORY NOTES

The entries in this volume are of two principal types, each accounting for about half of the total of 650 entries. The first type of entry gives general information on the hazardous behaviour of some recognisably discrete classes or groups of the almost 5000 individual compounds for which details are given in Volume 1, or of groups for which there may not be individual entries. Where possible, a general structural formula ranged right on the title line indicates the typical structure(s) of the members of each class of group of compounds. In these formulae, the following general symbols are used in addition to the usual symbols for the elements.

Ar = AROMATIC nucleus

E = NON-METALLIC element

M = METALLIC element

R = organic RESIDUE

X = HALOGEN

Z = non-halogen ANION species

Information on the derivation of the class and group names is given in the Introduction.

The second type of entry concerns reactive hazard topics, techniques or incidents which have a common theme or pattern of behaviour involving compounds of several different groups, so that no common structural feature exists for the compounds involved.

Substances not easily described as individual compounds of known empirical formula also appear in Volume II, constituting a third class of entries, which are essentually similar to a Volume I entry in nature.

The *ca.* 300 group-lists of compounds in the first type of entry serve as an index to analogues and homologues of a compound falling within the scope of the structural or behavioural group. Those compounds (congeners) of generally similar, but not identical structure to the majority in the group-lists are prefixed *. Flammable analogues are prefixed + to remind of the fire hazard. For flammable congeners,

the dagger prefix has taken precedence over the asterisk for the same reason. The order in the group-lists is alphabetic, rather than being order of empirical formulae as in the main text of Volume 1.

There is a full index to the the Volume 2 entry titles in Appendix 3. Appendix 4 contains the same entries classified on the basis of similarity in type of information content, as indicated by the bold sub-titles. This Appendix should be useful in locating reaction hazard information of a more general nature.

Details of corrections of typographical or factual errors, or of further items for inclusion in the text, will be welcomed, and a page which can be photocopied for this purpose will be found at the back of the book.

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ACCELERATING RATE CALORIMETRY (ARC)

1. Townsend, D. I. *et al.*, *Thermochim. Acta*, 1980, **37**, 1–30
2. Townsend, D. I., *Runaway Reactions*, 1981, Paper 3Q, 1–14
3. Coates, C. F., *Chem. & Ind.*, 1984, 212–216
4. Gibson, N., *Chem. & Ind.*, 1984, 209–212
5. *Explosion at the Dow Chemical Factory, King's Lynn, 27th June 1976*, London, HSE, 1977
6. Cardillo, P. *et al.*, *J. Haz. Mat.*, 1984, **9**, 221–234

Of the instrumental methods currently available for detailed small scale predictive investigation of hazardous and potentially hazardous reactions, the accelerating rate calorimeter appears to be the most sophisticated, sensitive, accurate and wide ranging in application. In essence the ARC maintains a sample in adiabatic condition once an exothermic reaction is detected, and then measures the consequent increases in temperature and pressure inside the sample holder in relation to elapsed time. The sample (1–5 g) is contained in a small spherical metal bomb, usable up to 500°C and 170 bar, within an insulated oven inside a massive steel containment vessel. The sample is heated on a stepped heat-wait-search programme until an exotherm is detected, when adiabatic conditions are then automatically established. The results can be processed to yield data relevant either to process control or reaction mechanism considerations. Fuller details of the theoretical background, construction and instrumentation, operation and capabilities of the technique have been published [1], and the theory behind the development of methods of estimating time to maximum rate of decomposition (TMR) from ARC results is discussed [2]. The place of ARC as part of a comprehensive hazard evaluation system in a chemical manufacturing context has been discussed [3]. The use of much simpler (and less expensive) Dewar flask methods for identifying potentially hazardous decompositions in reaction masses and powders has been compared and contrasted with ARC methods [4]. The part played by ARC in the investigation of the industrial explosions at King's Lynn (3,5-dinitro-2-toluamide) [5], and at Seveso (2,4,5-trichlorophenol) [6] shows the potential of the technique.

See ADIABATIC CALORIMETRY, CALORIMETRY, CHEMICAL STABILITY/REACTIVITY ASSESSMENT

ACCIDENTAL DECONTAMINATION

Kletz, T. A., *J. Loss Prev. Proc. Ind.*, 1989, **2**, 117

In a brief review of chemical accidents caused by accidental contamination of process materials, attention is drawn to the much less frequent opposite effect of accidental decontamination (or purification) as a cause of accidents. Some examples of the effects arising from accidental loss or inactivation of stabilisers or antioxidants from reactive materials are given.

See CATALYTIC IMPURITY INCIDENTS

ACCIDENT DATABASES

Database, Rugby, Institution of Chemical Engineers

MARS(Major Accident Reporting System) Database

Several organisations have lately established electronic databases, recording details of industrial chemical accidents. These should enable the user to learn from others mistakes and also establish a fixed version of accidents, which hitherto have changed in the retelling, and the more important have often been retold. The two above are examples of a wider trend. All tend to reflect the pre-occupations of their compilers, which are generally not so much the precise chemical causes of the mishap, but its effects.

ACETYLENIC COMPOUNDS C≡C

1. Davidsohn, W. E. *et al.*, *Chem. Rev.*, 1967, **67**, 74
2. Mushii, R. Ya. *et al.*, *Chem. Abs.*, 1967, **67**, 92449
3. Dutton, G. G. S., *Chem. Age*, 1947, **56**(1436), 11–13

The presence of the endothermic triply-bonded acetylene (ethyne) group confers explosive instability on a wide range of acetylenic compounds (notably when halogen is also present) and derivatives of metals (and especially of heavy metals) [1]. Explosive properties of butadiyne, buten-3-yne, hexatriyne, propyne and propadiene have been reviewed, with 74 references [2]. The tendency of higher acetylenes to explosive decomposition may be reduced by dilution with methanol [3]. The class includes the separately treated groups:

ACETYLENIC PEROXIDES
ALKYNES
COMPLEX ACETYLIDES
ETHOXYETHYNYL ALCOHOLS
HALOACETYLENE DERIVATIVES
METAL ACETYLIDES

DropBooks

and the individually indexed compounds:

Acetylenedicarboxaldehyde, 1403
Acetylenedicarboxylic acid, 1405
Azido-2-butyne, 1473
3-Azidopropyne, 1114
Benzyloxyacetylene, 3133
Bis(cyclopentadienyl)hexafluoro-2-butynechromium, 3636
Bis(dibutylborino)acetylene, 3775
Bis(dipropylborino)acetylene, 3670
Butoxyacetylene, 2428
2-Butyne-1,4-diol, 1526
2-Butyne-1-thiol, 1546
3-Butyn-1-yl 4-toluenesulfonate, 3399
N-Chloro-3-aminopropyne, 1129
1-Chloro-3.phenylpent-1-en-4-yn-3-ol, 3402
∗ 3-Cyanopropyne, 1416
1,2-Di(3-buten-1-ynyl)cyclobutane, 3509
Dibutyl-3-methyl-3-buten-1-ynlborane, 3618
Diethyl acetylenedicarboxylate, 2987

1-Diethylamino-1-buten-3-yne, 3020
cis-3,4-Diethynylcyclobut-3-ene-1,2-diol, 2921
2,4-Diethynyl-5-methylphenol, 3393
2,4-Diethynylphenol, 3244
1,10-Di(methanesulfonyloxy)deca-4,6-diyne, 3543
Dimethyl acetylenedicarboxylate, 2943
(Dimethylamino)acetylene, 1564
3,3-Dimethyl-1-nitro-1-butyne, 2395
Diphenylethyne, 3634
Di(1-propynyl) ether, 2326
Di(2-propynyl) ether, 2327
† Ethoxyacetylene, 1521
4-Ethoxy-2-methyl-3-butyn-2-ol, 2844
1-Ethoxy-2-propyne, 1909
2-Ethynylfuran, 2212
Ethynyl vinyl selenide, 1449
2-Heptyn-1-ol, 2841
4,5-Hexadien-2-yn-1-ol, 2328
2,4-Hexadiyne-1,6-dioic acid, 2094
2,5-Hexadiyn-1-ol, 2329
1,5-Hexadiyn-3-one, 2213
2,4-Hexadiynylene chloroformate, 2890
2,4-Hexadiynylene chlorosulfite, 2162
Lithium ethynediolate, 0993
† Methoxyacetylene, 1146
3-Methoxypropyne, 1523
† 2-Methyl-3-butyn-2-ol, 1910
2-Methyl-3,5,7-octatriyn-2-ol, 3135
3-Methyl-2-penten-4-yn-1-ol, 2384
1-(1-Methyl-1-phenylethyl)-4-(2-propynyloxy)benzene, 3760
† Methyl propiolate, 1442
2-Nitrophenylpropiolic acid, 3113
2-Nonen-4,6,8-triyn-1-al, 3112
Octacarbondioxide pentamer, 3904
Octacarbondioxide tetramer, 3884
Octatetrayne-1,8-dicarboxylic acid, 3235
Oligo(octacarbondioxide), 3108
1,3-Pentadiyne, 1825
2-Penten-4-yn-3-ol, 1879
Phenoxyacetylene, 2920
Phenyl, phenylethynyliodonium perchlorate, 3635
Poly(2,4-hexadiyne-1,6-ylene carbonate), 2669
Potassium acetylene-1,2-dioxide, 4934
Potassium ethynediolate, 0990
Potassium hydrogen acetylenedicarboxylate, 1382
Propiolaldehyde, 1085

Propiolic acid, 1086
Propioloyl chloride, 1065
3-Propynethiol, 1152
3-Propynol, 1147
5-(Prop-2-ynyloxy)-1,2,3,4-thiatriazole, 1420
2-Propynyl vinyl sulfide, 1883
Sodium ethynediolate, 1023
1,2:5,6:11,12:15,16-Tetrabenzocycloconta-1,5,11,15-tetraene-3,7,9,13,17,19-hexayne, 3888
Tetracyclo[20.2.0.$0^{6,9}$.$0^{4,17}$]tetracosa-1(22),6(9),14(17)-triene-2,4,10,12,18, 20-hexayne-7,8,15,16,23,24-hexone, 3858
1,3,5-Triethynylbenzene, 3443
∗ Triethynylphosphine, 2124

See also PEROXIDISABLE COMPOUNDS

Metals

Chemical Intermediates, 1972 Catalogue, 158, Tamaqua (Pa.), Air Products and Chemicals Inc., 1972

Acetylenic compounds with replaceable acetylenically bound hydrogen atoms must be kept out of contact with copper, silver, magnesium, mercury or alloys containing them, to avoid formation of explosive metal acetylides.

See METAL ACETYLIDES

ACETYLENIC PEROXIDES — C≡C−C−OOH

1. Milas, N. A. *et al*., *Chem. Eng. News*, 1959, **37**(37), 66
2. Milas, N. A. *et al*., *J. Amer. Chem. Soc*., 1952, **75**, 1472; 1953, **76**, 5970

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The importance of strict temperature control [1] to prevent explosion during the preparation [2] of acetylenic peroxides is stressed. Use of inert solvent to prevent undue increase in viscosity which leads to poor temperature control is recommended [1].

Individually indexed compounds are:
2-(4-Bromophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3709
2-(4-Chlorophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3711

See other PEROXIDES

ACID ANHYDRIDES — RCO.OCO.R, RSO_2OSO_2R

The several members of this reactive group involved in hazardous incidents are:
Acetic anhydride, 1534
Benzeneseleninic anhydride, 3495
Benzenesulfonic anhydride, 3498
∗ Chromium trioxide, 4242
Dichloromaleic anhydride, 1359
∗ Dinitrogen pentaoxide, 4748
Disulfur heptaoxide, 4870

∗ Disulfuryl dichloride, 4103
∗ Disulfuryl difluoride, 4326
∗ Methaneboronic anhydride–pyridine complex, 0427
∗ Peroxypropionyl nitrate, 1187
∗ Peroxypropionyl perchlorate, 1167
Phthalic anhydride, 2899
∗ Pivaloyloxydiethylborane, 3198
† Propadiene-1,3-dione, 1349
Succinic anhydride, 1443
Sulfur trioxide, 4849
∗ Sulfur trioxide–dimethylformamide, 4850
Tetraphosphorus decaoxide, 4872
Trifluoroacetic anhydride, 1366
Trifluoroacetyl trifluoromethanesulfonate, 1057

ACRYLIC MONOMERS $CH_2{=}C(X)C{=}O$

Schulze, S. *et al., Chem. Eng. Technol*, 1998, **21**, 829
Most of these monomers are inclined to violent polymerisation unless stabilised. Stabilisation usually involves oxygen as well as the nominal stabiliser. A kinetic study of the process for acrylic and methacrylic acids is reported.
See VIOLENT POLYMERISATION
See also POLYMERISATION INCIDENTS

ACYL AZIDES $RCO.N_3$, $-SO_2N_3$, $-P(O)N_3$

1. Smith, P. A. S., *Org. React.*, 1946, **3**, 373–375
2. Houben-Weyl, 1952, Vol. 8, 680
3. Lieber, E. *et al., Chem. Rev.*, 1965, **65**, 377
4. Balabanov, G. P. *et al., Chem. Abs.*, 1969, **70**, 59427
5. Renfrow, W. B. *et al., J. Org. Chem.*, 1975, **40**, 1526
6. Anon., *Sichere Chemiarb.*, 1984, **36**, 143–144
7. Hazen, G. G. *et al., Synth. Comm.*, 1981, **11**(12), 947
8. Tuma, L. D. *Thermochim. Acta.*, 1994, 243(2) 161

Azides of low molecular weight (more than 25% nitrogen content) should not be isolated from solution, as the concentrated material is likely to be dangerously explosive [1]. The concentration of such solutions (prepared below 10°C) should be <10% [2]. Carbonyl azides are explosive compounds, some exceptionally so, and suitable handling precautions are necessary [3]. The sensitivity to friction, heat and impact of benzenesulfonyl azide, its 4-chloro-, methyl-, methoxy-, methoxycarbonylamino-, and nitro-derivatives, and 1,3-benzenedisulfonyl diazide were studied [4]. Benzenesulfonyl azide and 2-toluenesulfonyl azide may be smoothly thermolysed in benzene [5]. In this Curtius procedure for rearrangement with loss of nitrogen to isocyanates, it is important to ensure (by IR examination) that the products of such rearrangements are substantially free of residual acyl azide before attempting distillation of the material. Failure to make this check led to a

violent explosion of 70 g of an unspecified crude isocyanate when the distillation flask was immersed in a preheated oil-bath [6]. Further mishaps have provoked further studies: Tests for safety as reagents for azo transfer were conducted on five arylsulfonyl azides. It was concluded that toluenesulfonyl azide (with the lowest molecular weight) was the least safe, of shock sensitivity and power variously compared with TNT and tetryl (and elsewhere with nitroglycerine). [Such power seems thermodynamically implausible, it is assigned only 80 kcal/mole, 1.7 kJ/g.] The safest was 4-dodecylbenzenesulfonyl azide (with the highest m.w.). Thermally most stable was 4-carboxybenzenesulfonylazide, but its decomposition rate was highest once started, it was marginally shock sensitive [7]. Another safety study of sulfonyl azides. including detonation, also preferred dodecylbenzenesulfonyl azide [8]. Individually indexed compounds are:

Acetyl azide, 0771
N-Azidocarbonylazepine, 2728
Azidocarbonyl fluoride, 0339
∗ Azidocarbonylguanidine, 0820
4-Azidocarbonyl-1,2,3-thiadiazole, 1069
Azidodithioformic acid, 0386
Benzene-1,3-bis(sulfonyl azide), 2210
Benzenesulfinyl azide, 2273
Benzenesulfonyl azide, 2274
Benzoyl azide, 2698
4,4′-Biphenylene-bis-sulfonylazide, 3468
cis-1,2-Bis(azidocarbonyl)cyclobutane, 2323
1,2-Bis(azidocarbonyl)cyclopropane, 1835
Bis(azidothiocarbonyl) disulfide, 1016
4-Bromobenzoyl azide, 2644
N-Butylamidosulfuryl azide, 1693
tert-Butyl azidoformate, 1936
Carbonic diazide, 0550
Carboxybenzenesulfonyl azide, 2699
4-Chlorobenzenesulfonyl azide, 2152
4-Chlorobenzoyl azide, 2654
N-(2-Chloroethyl)-*N*-nitrosocarbamoyl azide, 1131
Cyanodiazoacetyl azide, 1346
Cyanohydrazonoacetyl azide, 1083
1,2-Diazidocarbonylhydrazine, 0720
Diazoacetyl azide, 0679
Disulfuryl diazide, 4780
Ethyl azidoformate, 1193
Fluorothiophosphoryl diazide, 4308
2-Furoyl azide, 1821
Glutaryl diazide, 1874
4-Methylaminobenzene-1,3-bis(sulfonyl azide), 2785
4-Nitrobenzenesulfinyl azide, 2204
Palladium(II) azidodithioformate, 1015

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Phenylphosphonic azide chloride, 2233
Phenylphosphonic diazide, 2284
3-Phenylpropionyl azide, 3144
Phenylthiophosphonic diazide, 2285
Phthaloyl diazide, 2898
Pivaloyl azide, 1935
Potassium azidodisulfate, 4655
Potassium azidosulfate, 4653
6-Quinolinecarbonyl azide, 3243
∗ Silver azidodithioformate, 0303
Sodium azidosulfate, 4759
Succinoyl diazide, 1438
Sulfamoyl azide, 4472
Sulfinyl azide, 4778
Sulfuryl azide chloride, 4031
Sulfuryl diazide, 4779
∗ Thallium(I) azidodithiocarbonate, 0543
4-Toluenesulfinyl azide, 2780
4-Toluenesulfonyl azide, 2781
Trifluoroacetyl azide, 0627
N-(Trifluoromethylsulfinyl)trifluoromethylimidosulfinyl azide, 0640
Trifluoromethylsulfonyl azide, 0348
1,3,5-Tris(4-azidosulfonylphenyl)-1,3,5-triazinetrione, 3818

See also 2-AZIDOCARBONYL COMPOUNDS, CUBANES, SULFINYL AZIDES

ACYL CHLORIDES — RCO.Cl

Aromatic hydrocarbons, Trifluoromethanesulfonic acid
See Trifluoromethanesulfonic acid: Acyl chlorides, etc.

ACYL HALIDES — RCO.X, -SO.X, -SO_2X

This group tends to react violently with protic organic solvents, water, and the aprotic solvents, dimethylformamide and dimethyl sulfoxide. Their facile reaction with ethers is also potentially hazardous.
See Propionyl chloride: Diisopropyl ether

Individually indexed compounds are:
Acetyl bromide, 0728
† Acetyl chloride, 0735
† Acryloyl chloride, 1093
Azidocarbonyl fluoride, 0339
Benzenesulfinyl chloride, 2234
Benzenesulfonyl chloride, 2235
Benzoyl chloride, 2675
∗ Benzyl chloroformate, 2931

tert-Butyl chloroperoxyformate, 1926
† Butyryl chloride, 1555
∗ Carbonyl dichloride, 0329
∗ Carbonyl difluoride, 0343
∗ Chlorine fluorosulfate, 3975
(Chlorocarbonyl)imidosulfur difluoride, 0318
N-(Chlorocarbonyloxy)trimethylurea, 1924
∗ Chlorosulfonyl isocyanate, 0324
Chlorosulfuric acid, 3997
∗ Chromyl fluorosulfate, 4225
Cyanoacetyl chloride, 1075
Cyanoformyl chloride, 0600
4,4-Diferrocenylpentanoyl chloride, 3859
2,2-Dinitro-2-fluoroethoxycarbonyl chloride, 1072
Disulfuryl dichloride, 4103
Disulfuryl difluoride, 4326
† Ethyl chloroformate, 1164
Ethyl oxalyl chloride, 1456
N-Ethyl-*N*-propylcarbamoyl chloride, 2468
∗ Fluorine fluorosulfate, 4324
Furoyl chloride, 1818
2,4-Hexadiynylene chloroformate, 2890
2,4-Hexadiynylene chlorosulfite, 2162
† Isobutyryl chloride, 1558
Isophthaloyl chloride, 2888
† Isopropyl chloroformate, 1560
Methanesulfinyl chloride, 0435
Methoxyacetyl chloride, 1165
4-Methoxybenzoyl chloride, 2930
† Methyl chloroformate, 0599
Oleoyl chloride, 3772
Oxalyl dibromide, 0583
Oxalyl dichloride, 0605
∗ Oxopropanedinitrile, 1341
Pentafluoropropionyl fluoride, 1054
Peroxodisulfuryl difluoride, 4328
∗ Phenylphosphonyl dichloride, 2245
† Pivaloyl chloride, 1925
Propioloyl chloride, 1065
† Propionyl chloride, 1163
Sebacoyl chloride, 3341
Sulfinyl chloride, 4096
Sulfonyl chloride, 4099
Sulfur oxide-(*N*-fluorosulfonyl)imide, 4305
Sulfuryl azide chloride, 4031
Terephthaloyl chloride, 2880

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∗ 2,4,6-Trichloro-1,3,5-triazine, 1038
Trifluoroacryloyl fluoride, 1049
Trifluoromethanesulfenyl chloride, 0322
Trifluoromethanesulfinyl fluoride, 0354

O-ACYLHYDROXAMIC ACIDS HOC(R)=NOCOR′

Houben Weyl 10/4, 1968, 232
Warning is given against dry distillation of the alkali salts as an isocyanate preparation. The decomposition is often explosive
See other N–O COMPOUNDS

ACYL HYPOHALITES RCO.OX

1. Tari, I. *et al.*, *Inorg. Chem.*, 1979, **18**, 3205–3208
2. Skell, P. S. *et al.*, *J. Amer. Chem. Soc.*, 1983, **105**, 4000, 4007

Sodium salts of fluoroacids react with chlorine fluoride at −112 to −78°C to give explosively unstable fluoroacyl hypochlorites. Trifluoroacetyl hypochlorite and its pentafluoropropionyl, heptafluorobutyryl, difluoroacetyl and chlorodifluoroacetyl analogues explode without fail if the partial pressure exceeds 27–67 mbar. Hexafluoroglutaryl dihypochlorite explodes above −10°C [1]. Of the 4 compounds prepared, acetyl, propionyl, isobutyryl and pivaloyl hypobromites, the 2 latter appeared stable indefinitely at −41°C in the dark, while the 2 former exploded unpredictably as isolated solids [2].
See Acetyl hypobromite, Propionyl hypobromite

Individually indexed compounds are:
Acetyl hypobromite, 0729
Acetyl hypofluorite, 0751
Caesium fluoroxysulfate, 4256
Chlorodifluoroacetyl hypochlorite, 0603
Difluoroacetyl hypochlorite, 0653
Fluorine fluorosulfate, 4324
Heptafluorobutyryl hypochlorite, 1352
Heptafluorobutyryl hypofluorite, 1369
Hexafluoroglutaryl dihypochlorite, 1806
Pentafluoropropionyl hypochlorite, 1034
Pentafluoropropionyl hypofluorite, 1056
Propionyl hypobromite, 1154
Rubidium fluoroxysulfate, 4309
Trifluoroacetyl hypochlorite, 0594
Trifluoroacetyl hypofluorite, 0633

ACYL NITRATES $RCO.ONO_2$

A thermally unstable group of compounds, tending to violent decomposition or explosion on heating. Individually indexed compounds are:

Acetyl nitrate, 0765
Benzoyl nitrate, 2689
Butyryl nitrate, 1573
3-Nitrobenzoyl nitrate, 2664
∗ Peroxyacetyl nitrate, 0766
∗ Peroxypropionyl nitrate, 1187
See Nitric acid: Phthalic anhydride, etc., 4436

ACYL NITRITES **RCO.ON:O**

1. Ferrario, E., *Gazz. Chim. Ital. [2]*, 1901, **40**, 98–99
2. Francesconi, L. *et al., Gazz. Chim. Ital. [1]*, 1895, **34**, 442

The stabilities of propionyl nitrite and butyryl nitrite are greater than that of acetyl nitrite, butyryl nitrite being the least explosive of these homologues [1]. Benzyl nitrite is also unstable [2]. Individual compounds are:
Acetyl nitrite, 0762
Heptafluorobutyryl nitrite, 1368
Propionyl nitrite, 1185
Trifluoroacetyl nitrite, 0626
See Sodium nitrite: Phthalic acid, etc., 4720

ADHESIVE LABELS

Tolson, P. *et al., J. Electrost.*, 1993, **30**, 149

A heavy duty lead-acid battery exploded when an operator peeled an adhesive label from it. Investigation showed that this could generate>8 kV potential. Discharge through the hydrogen/oxygen headspace consequent upon recharging batteries caused the explosion. The editor has remarked very vivid discharges when opening Chemical Society self-adhesive envelopes.
See STATIC INITIATION INCIDENTS

DropBooks

ADIABATIC CALORIMETRY

1. Hub, L., *Runaway Reactions*, 1981, Paper 3/K, 1–11
2. Hakl, J., *Runaway Reactions*, 1981, Paper 3/L, 1–11
3. Brogli, F. *et al.*, *Runaway Reactions*, 1981, Paper 3/M, 1–10
4. Townsend, D. I., *Runaway Reactions*, 1981, Paper 3/Q, 1–14
5. Cardillo, P. *et al., J. Haz. Mat.*, 1984, **9**, 224

The Sikarex safety calorimeter system and its application to determine the course of adiabatic self-heating processes, starting temperatures for self-heating reactions, time to explosion, kinetic data, and simulation of real processes, are discussed with examples [1]. The Sedex (sensitive detection of exothermic processes) calorimeter uses a special oven to heat a variety of containers with sophisticated control and detection equipment, which permits several samples to be examined simultaneously [2]. The bench-scale heat-flow calorimeter is designed to provide data specifically oriented towards processing safety requirements, and a new computerised design

has become available [3]. The accelerating rate calorimeter is the most sophisticated and sensitive of the techniques, and it is claimed that very close parallels with large-scale process operations can be simulated [4].

See ACCELERATING RATE CALORIMETRY, ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY, HEAT FLOW CALORIMETRY

AGITATION INCIDENTS

Weir, D. E., *Plant/Oper. Progr.*, 1986, **5**, 142–147

The relationship of agitation problems (failure, incomplete mixing, shear energy input) with thermal runaway reactions and ways of avoiding these, are discussed.

Several of the runaway reactions or violent incidents in the main text were caused by ineffective agitation or by the complete absence of agitation, particularly in reactions between 2 phases of widely differing densities. Individual cases involved are:

2-Chloronitrobenzene, 2141
Chromyl chloride, 4054
Diethyl 4-nitrophenyl thionophosphate, 3328
Ethylmagnesium iodide, 0859
Hydrogen peroxide, : Iron(II) sulfate, 2-Methylpyridine, Sulfuric acid, 4477
Lead(IV) oxide, : Carbon black, Chlorinated paraffin, Manganese(IV) oxide, 4834
Lithium tetrahydroaluminate, : Fluoroamides, 0075
4-Methyl-2-nitrophenol, 2767
Nitric acid, : *tert*-Butyl-*m*-xylene, Sulfuric acid, 4436
Nitric acid, : 2-Formylamino-1-phenyl-1,3-propanediol, 4436
Nitric acid, : Hydrocarbons, 4436
Nitric acid, : Nitrobenzene, Sulfuric acid, 4436
Nitric acid, : 1-Nitronaphthalene, Sulfuric acid, 4436
2-Nitrotoluene, : Alkali, 2763
Phosphorus tribromide, : Phenylpropanol, 0293
Potassium hydroxide, : Water, 4428
Sodium carbonate, 0552
Sodium dichromate, : Sulfuric acid, Trinitrotoluene, 4250
Sodium hydrogen carbonate, : Carbon, Water, 0390
Sulfinyl chloride, : Tetrahydrofuran, 4096
Sulfuric acid, : 2-Aminoethanol, 4479
Sulfuric acid, : 4-Methylpyridine, 4479
Tetrachlorosilane, : Ethanol, Water, 4173

See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

AIR

1. Anon., *Site Safe News*, 1991, Summer, (HSE, Bootle, UK)
2. Allan, M., *CHAS Notes*, 1991, **IX**(5), 2
3. Sagan, C. *et al.*, *Nature*, 1993, **365**(6448), 720

A dangerous oxidant by virtue of its oxygen content, responsible for almost all fires, dust and vapour-cloud explosions, and for many other incidents. When heated to decomposition, air produces fumes of highly toxic nitrogen oxides. Air is frequently encountered compressed in combustible containers (tyres) which can explode with fatal results. Sometimes combustion seems to be the cause of the burst, this may be attributed to excessive heating and prior decomposition reactions generating a gaseous fuel [1]. Another fuel source causing a similar burst was an emergency inflator powered by liquid propane/butane [2].

The editor has been told that air can be explosive in its own right in a eucalyptus wood on a hot day, and, having smelt one, does not find this absolutely incredible. Explosive air is sometimes also found in caves and mines when decaying vegetable matter is present.

From a theoretical and thermodynamic standpoint, air should be considered a poison to carbon-based life [3]. Handle with due caution.

See also BATS, DIESEL ENGINES

ALDEHYDES **RCO.H**

1. Editor's comments, 1995
2. Britton, L. B. *Process Saf. Progr.*, 1998, **17**(2), 138

These materials are very easily autoxidised and often have a low autoignition temperature. It is reported that many of the less volatile liquid aldehydes will eventually inflame if left exposed to air on an absorbent surface. The mechanism is undoubtedly similar to that giving rise to easy ignition in the air-oxidation of acetaldehyde and propionaldehyde; initial formation of a peroxy-acid which catalyses the further oxidation[1]. Autoignition temperatures of lower aldehydes are much reduced by pressure, but appear to depend little on oxygen content. The effect is worst in the presence of free liquid, in which initial oxidation appears to occur, possibly catalysed by iron, followed by ignition of the vapour phase [2]. An acetaldehyde/rust mix exploded at room temperature on increasing the air pressure to 7 bar.

See Acetaldehyde

Individually indexed compounds are:

† Acetaldehyde, 0828
4-Acetoxy-3-methoxybenzaldehyde, 3290
4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3266
† Acrylaldehyde, 1145
4-Azidobenzaldehyde, 2697
† Benzaldehyde, 2731
† Butyraldehyde, 1607
∗ Chloroacetaldehyde oxime, 0787
2-Chloro-6-nitrobenzaldehyde, 2650
4-Chloro-3-nitrobenzaldehyde, 2651
5-Chloro-2-nitrobenzaldehyde, 2652
Cinnamaldehyde, 3134

DrooBooks

† Crotonaldehyde, 1516
† 2-Ethylhexanal, 3050
† Formaldehyde, 0416
2-Furaldehyde, 1836
4-Hydroxy-3-methoxybenzaldehyde, 2958
3-Hydroxy-4-nitrobenzaldehyde, 2690
4-Hydroxy-3-nitrobenzaldehyde, 2691
2-Indanecarboxaldehyde, 3288
† Isobutyraldehyde, 1611
† Isovaleraldehyde, 1958
† Methacrylaldehyde, 1522
4-Methoxybenzaldehyde, 2956
3-Methoxy-2-nitrobenzaldehyde, 2937
∗ 2-Nitroacetaldehyde oxime, 0809
2-Nitroacetaldehyde
3-Nitrobenzaldehyde, 2687
4-Nitrobenzaldehyde, 2688
Paraformaldehyde, 0417
α-Pentylcinnamaldehyde, 3663
Propionaldehyde, 1224
Tridecanal, 3619
† Valeraldehyde, 1966

See also PEROXIDISABLE COMPOUNDS, INSULATION, PAPER TOWELS

ALKALI-METAL ALLOYS

1. Mumford, C., *Chem. Brit.*, 1978, **14**, 170
2. Ingham, P. L., *Chem. Brit.*, 1978, **14**, 326
3. Bretherick, L., *Chem. Brit.*, 1978, **14**, 426
4. Sloan, S. A., *Chem. Brit.*, 1978, **14**, 597

In response to a statement [1] that alloys of 2 alkali-metals (Li−Na, K−Na) can be prepared in small amounts by beating the solid components together, without heating in the latter case, it was emphasised that the real hazard arises not from reaction of the surface coating of potassium superoxide with potassium, but with residues of oil or organic matter on the potassium which will explode under impaction with the superoxide [2]– [4].

See Potassium (*Slow oxidation*) *also* ALKALI METALS, below

ALKALI-METAL DERIVATIVES OF HYDROCARBONS RM, ArM

1. Sidgwick, 1950, 68, 75
2. Leleu, *Cahiers*, 1977(88), 370

Alkali-metal derivatives of aliphatic or aromatic hydrocarbons, such as methyllithium, ethylsodium or phenylpotassium, are the most reactive towards moisture and air, immediately igniting in the latter. Derivatives of benzyl compounds, such as benzylsodium, are of slightly lower activity, usually but not always igniting in

air. Derivatives of hydrocarbons with definitely acidic hydrogen atoms (acetylene, phenylacetylene, cyclopentadiene, fluorene), though readily oxidised, are usually relatively stable in ambient air. Sodium phenylacetylide if moist with ether, ignites; derivatives of triphenylmethane also when dry [1]. Biphenyl-, naphthyl-, anthryl- and phenanthryl-sodium may all ignite in air when finely divided, and all react violently with water [2].

Specific compounds may be found in the groups:

See also ALKYLMETALS, ARYLMETALS, ORGANOMETALLICS

ALKALI METALS

1. *Handling and Uses of the Alkali Metals* (Advances in Chemistry Series No. 19), Washington, ACS, 1957
2. Markowitz, M. M., *J. Chem. Educ.*, 1963, **40**, 633–636
3. *Alkali Metal Dispersions*, Fatt, I. *et al.*, London, Van Nostrand, 1961
4. John, G. D., *School Sci. Rev.*, 1980, **62**(219), 279–286

The collected papers of a symposium at Dallas, April 1956, cover all aspects of the handling, use and hazards of lithium, sodium, potassium, their alloys, oxides and hydrides, in 19 chapters [1]. Interaction of all 5 alkali metals with water under various circumstances has been discussed comparatively [2]. In a monograph covering properties, preparation, handling and applications of the enhanced reactivity of metals dispersed finely in hydrocarbon diluents, the hazardous nature of potassium dispersions, and especially of rubidium and caesium dispersions is stressed [3]. Alkaline-earth metal dispersions are of relatively low hazard. Safety practices for small-scale storage, handling, heating and reactions of lithium potassium and sodium with water are reviewed [4].

See Potassium (reference 6)

DropBooks

ALKANETHIOLS **RSH**

Ethylene oxide

See Ethylene oxide: Alkanethiols

Nitric acid

See Nitric acid: Alkanethiols

Individually indexed compounds are:

† Butanethiol, 1712
† 2-Butanethiol, 1713
Dodecanethiol, 3567
† Ethanethiol, 0933
† Methanethiol, 0489
† 2-Methylbutane-2-thiol, 2023
† 3-Methylbutanethiol, 2024
† 2-Methylpropanethiol, 1715
† 2-Methyl-2-propanethiol, 1716

† Pentanethiol, 2025
† Propanethiol, 1289
† 2-Propanethiol, 1290

ALKENEBIS(SULFONIUM PERCHLORATES) $R_2S^+-C=C-S+R_2\ 2ClO_4$

Shine, H. J. *et al., J. Org. Chem.*, 1979, **44**, 915–917
The perchlorate salts of the bis-adducts of thianthrene (X = S) or phenoxathiin (X = O) with substituted acetylenes explode on heating.
See Thianthrenium perchlorate *See other* NON-METAL PERCHLORATES

ALKENES $-C=C-$

Oxides of nitrogen
Simmons, H. E. *et al., Chem. Eng. News*, 1995, **73**(32), 4
Several nitrogen oxides; dinitrogen trioxide, dinitrogen tetroxide and dinitrogen pentoxide; can readily add to alkenes; the resultant nitronitroso-dinitro- and nitronitrato-alkanes will be explosive if of low molecular weight and impurities make them more so. The tendency of nitroso compounds to exist as insoluble dimers, which precipitate and thus concentrate, makes dinitrogen trioxide a more hazardous contaminant than its higher homologues.
See Nitrogen oxide: Dienes, Oxygen
See 2-Chloro-1,3-butadiene: Preparative hazard
† 1-Butene, 1577
† *cis*-2-Butene, 1578
† *trans*-2-Butene, 1623
∗ Δ 3-Carene, 3336
† Cyclobutene, 1483
cis-Cyclododecene, 3351
† Cycloheptene, 2837
† Cyclohexene, 2406
† Cyclopentene, 1891
∗ 2-Deuterobicyclo[2.2.1]hept-2-ene, 2811
† 2,6-Dimethyl-3-heptene, 3190
∗ 1,1-Diphenylethylene
∗ *trans*-1,2-Diphenylethylene
† Ethylene, 0781
† 1-Heptene, 2851
† 2-Heptene, 2852
† 3-Heptene, 2853
† 1-Hexene, 2459
† 2-Hexene, 2460
† 4-Methylcyclohexene, 2839
† 2-Methyl-1-pentene, 2462
† 4-Methyl-1-pentene, 2463

† *cis*-4-Methyl-2-pentene, 2464
† *trans*-4-Methyl-2-pentene, 2465
† 2-Methylpropene, 1582
† 1-Octene, 3040
† 2-Octene, 3041
∗ 2-Pinene, 3339
† Propene
∗ 1-Pyrrolidinylcyclohexene, 3350
∗ Styrene, 2945
† 2,3,3-Trimethylbutene, 2855
† 2,3,4-Trimethyl-1-pentene, 3042
† 2,3,4-Trimethyl-2-pentene, 3044
† 2,4,4-Trimethyl-1-pentene, 3043
† 2,4,4-Trimethyl-2-pentene, 3045
† 3,4,4-Trimethyl-2-pentene, 3046
† Vinylcyclohexane, 3026

ALKENYL NITRATES —C=C—ONO_2

Tetrafluorohydrazine
See Tetrafluorohydrazine: Alkenyl nitrates
See related ALKYL NITRATES

ALKYLALUMINIUM ALKOXIDES AND HYDRIDES R_2AlOR', R_2AlH

Although substitution of a hydrogen atom or an alkoxy group for one alkyl group in a trialkylaluminium tends to increase stability and reduce reactivity and the tendency to ignition, these compounds are still of high potential hazard, the hydrides being used industrially as powerful reducants.
See ALKYLALUMINIUM DERIVATIVES (references 1,3,6)

Ethers
Wissink, H. G., *Chem. Eng. News*, 1997, **75**(9), 6
Dialkylaluminium hydrides can cleave lower ethers to generate gaseous products (hydrocarbons and/or hydrogen), which may pressurise and burst containers if solutions in ethers be stored.

Individually indexed compounds of this relatively small sub-group of commercially available compounds are:
Diethylaluminium hydride, 1719
Diethylethoxyaluminium, 2554
Diisobutylaluminium hydride, 3082
Dimethylaluminium hydride, 0936
Dipropylaluminium hydride, 2552
∗ 4-Ethoxybutyldiethylaluminium, 3372
Ethoxydiisobutylaluminium, 3373

PropBooks

Tetramethyldialuminium dihydride, 1778
∗ Triethoxydialuminium tribromide, 2555

ALKYLALUMINIUM DERIVATIVES

1. Mirviss, S. B. *et al., Ind. Eng. Chem.*, 1961, **53**(1), 53A −56A
2. Heck, W. B. *et al., Ind. Eng. Chem.*, 1962, **54**(12), 35−38
3. Kirk-Othmer, 1963, Vol. 2, 38, 40
4. Houben-Weyl, 1970, Vol. 13.4, 19
5. 'Aluminium Alkyls', Brochure PB 3500/1 New 568, New York, Ethyl Corp., 1968
6. 'Aluminium Alkyls', New York, Texas Alkyls, 1971
7. Knap, J. E. *et al., Ind. Eng. Chem.*, 1957, **49**, 875
8. Thomas, W. H., *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**(1), 120−122
9. Van Vliet, M. R. P. *et al., Organometallics*, 1987, **6**, 1652−1654

This main class of ALKYLALUMINIUM DERIVATIVES is divided for structural convenience into the 3 groups: TRIALKYLALUMINIUMS; ALKYLALUMINIUM ALKOXIDES AND HYDRIDES; and ALKYLALUMINIUM HALIDES.

Individual compounds are indexed under their appropriate group titles, but since most of the available compounds are liquids with similar hazardous properties, these will be described collectively here. These aspects of the class have been extensively reviewed and documented [1,2,3,4,5,6,7,8].

Compounds with alkyl groups of C_4 and below all ignite immediately on exposure to air, unless diluted with a hydrocarbon solvent to 10−20% concentration [6]. Even these solutions may ignite on prolonged exposure to air, owing to exothermic autoxidation, which becomes rapid if solutions are spilled (high surface:volume ratio) [2,6]. Compounds with C_5−C_{14}alkyl groups (safe at 20−30% conc.) smoke in air but do not burn unless ignited externally or if the air is very moist. Contact with air enriched with oxygen above the normal 21% content will cause explosive oxidation to occur.

Fires involving alkylaluminium compounds are difficult to control and must be treated appropriately to particular circumstances [1,5,6], usually with dry-powder extinguishers. Halocarbon fire extinguishants (carbon tetrachloride, chlorobromomethane, etc.), water or water-based foam must not be applied to alkylaluminium fires. Carbon dioxide is ineffective unless dilute solutions are involved [5,6]. Suitable handling and disposal procedures have been detailed for both laboratory [1,2,5,6,7] and manufacturing [5,6] scales of operation.

See TRIALKYLALUMINIUMS
See ALKYLALUMINIUM ALKOXIDES AND HYDRIDES
See ALKYLALUMINIUM HALIDES

Alcohols

Alkylaluminium derivatives up to C_4 react explosively with methanol or ethanol, and triethylaluminium also with 2-propanol.

Halocarbons

With the exception of chlorobenzene and 1,2-dichloroethane, halocarbon solvents are unsuitable diluents, as carbon tetrachloride and chloroform may react violently with alkylaluminium derivatives. The hazards of individually mixing 7 alkylaluminiums with 7 chlorinated solvents have been assessed comparatively. Most of a series of cyclic coordination complexes between triethylaluminium and α-iminoketones decomposed violently when dissolved in halogenated solvents.

Oxidants

In view of the generally powerfully reducing properties of alkylaluminium derivatives, deliberate contact with known oxidants must be under careful control with appropriate precautions.

Water

Interaction of alkylaluminium derivatives up to C_9 chain length with liquid water is explosive and violent shock effects have been noted [4].

See other ALKYLMETAL HALIDES, ALKYLMETAL HYDRIDES, ALKYLMETALS

ALKYLALUMINIUM HALIDES $RAlX_2$, R_2AlX, $R_3Al.AlX_3$

Three main structural sub-groups can be recognised: alkylaluminium dihalides, dialkylaluminium halides, and trialkyldialuminium trihalides (equimolar complexes of a trialkylaluminium and an aluminium trihalide). While this is generally a very reactive group of compounds, similar in reactivity to trialkylaluminium compounds, increase in size of the alkyl groups present and in the degree of halogen substitution tends to reduce pyrophoricity.

See ALKYLALUMINIUM DERIVATIVES (references 1,2)

DropBooks

Individually indexed compounds of this group many of which are commercially available in bulk are:

Diethylaluminium bromide, 1670
Diethylaluminium chloride, 1671
Diisobutylaluminium chloride, 3064
Dimethylaluminium bromide, 0882
Dimethylaluminium chloride, 0883
Ethylaluminium bromide iodide, 0841
Ethylaluminium dibromide, 0842
Ethylaluminium dichloride, 0843
Ethylaluminium diiodide, 0844
∗ Hexaethyltrialuminium trithiocyanate, 3695
Methylaluminium diiodide, 0423
Triethyldialuminium trichloride, 2556
Trimethyldialuminium trichloride, 2556

See other ALKYLMETAL HALIDES

ALKYLBORANES **RBH_2, R_2BH, R_3B**

1. Sidgwick, 1950, 371
2. Mirviss, S. B. *et al., Ind. Eng. Chem.*, 1961, **53**(1), 53A
3. Brown, H. C. *et al., Tetrahedron*, 1986, **42**, 5523–5530

Trimethylborane and triethylborane ignite in air, and tributylborane ignites in a thinly diffused layer, as when poured on cloth [1]. Generally, the pyrophoric tendency of trialkylboranes decreases with increasing branching on the 2- and 3-carbon atoms of the alkyl substituent(s) [2]. Reaction of a trialkylborane with oxygen under controlled, mild and safe conditions gives high yields of the corresponding alkanols [3].

Individually indexed compounds are:
Bis(dibutylborino)acetylene, 3775
∗ *N,N′*-Bis(diethylboryl)methylamine, 3223
Bis(dipropylborino)acetylene, 3670
Dibutyl-3-methyl-3-buten-1-ynlborane, 3618
† 1,2-Dimethylborane, 0961
† 1,1-Dimethyldiborane, 0960
Ethylpentaborane(9), 0973
∗ Methylborylene, 0425
Methyldiborane, 0513
∗ Perhydro-9*b*-boraphenalene, 3550
∗ 1-Phenylboralane, 3317
∗ Pivaloyloxydiethylborane, 3198
'Tetraethyldiborane', 3098
Tetramethyldiborane, 1779
'Tetrapropyldiborane', 3580
Tri-2-butylborane, 3570
mixo-Tributylborane, 3569
Triethylborane, 2559
Triethyldiborane, 2588
Trimethylborane, 1295
Trimethyldiborane, 1334
Tripropylborane, 3217
∗ Tris(dimethylfluorosilylmethyl)borane, 3224

See other ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

ALKYL CHLORITES **ROCl:O**

Chlorite esters, like chlorite salts, are explosively unstable.

See Silver chlorite, Alone, or Iodoalkanes

See also CHLORITE SALTS

ALKYLHALOBORANES **RBX_2, R_2BX**

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

∗ Bis(difluoroboryl)methane, 0394
Bromodimethylborane, 0887
Butyldichloroborane, 1629
Chlorodibutylborane, 3065
Chlorodiethylborane, 1673
Chlorodipropylborane, 2534
Dibromomethylborane, 0426
Dichloroethylborane, 0845
∗ Dichlorophenylborane, 2222
See other ALKYLNON-METAL HALIDES

ALKYLHALOPHOSPHINES **RPX_2, R_2PX**

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

∗ 1,2-Bis(dichlorophosphino)ethane, 0797
Bis(trifluoromethyl)chlorophosphine, 0597
∗ Bis(trifluoromethyl)cyanophosphine, 1053
tert-Butyldifluorophosphine, 1646
Chlorodimethylphosphine, 0899
Di-*tert*-butylfluorophosphine, 3067
Dichloromethylphosphine, 0438
Difluorotrifluoromethylphosphine, 0361
Difluorotrifluoromethylphosphine oxide, 0360
Fluorobis(trifluoromethyl)phosphine, 0646
∗ Fluorobis(trifluoromethyl)phosphine oxide, 0645
∗ Tetrachlorotrifluoromethylphosphorane, 0333
See other ALKYLNON-METAL HALIDES

DropBooks

ALKYLHALOSILANES **$RSiX_3$, $RSiHX_2$, R_2SiX_2, R_2SiHX, R_3SiX**

As with other non-metal derivatives, reactivity depends on chain-length, branching and degree of halogen substitution. Individually indexed compounds are:

† Chloromethylphenylsilane, 2810
† Chlorotrimethylsilane, 1304
† Cyanotrimethylsilane, 1665
† Dichlorodiethylsilane, 1683
† Dichlorodimethylsilane, 0902
† Dichloroethylsilane, 0903
† Dichloromethylsilane, 0470
† Dichloromethylvinylsilane, 1208
† Iodotrimethylsilane, 1306
† Methyltrichlorosilane, 0439
† Trichloroethylsilane, 0854
† Trichlorovinylsilane, 0746
∗ Tris(dimethylfluorosilylmethyl)borane, 3224
See other ALKYLNON-METAL HALIDES

Swern, 1970, Vol. 1, 19; 1971, Vol. 2, 1, 29

Most alkylhydroperoxides are liquid, the explosivity of the lower members (possibly owing to presence of traces of the dialkyl peroxides) decreasing with increasing chain length.

Transition metal complexes

Skibida, I. P., *Russ. Chem. Rev.*, 1975, 789–800

The kinetics and mechanism of decomposition of organic hydroperoxides in presence of transition metal complexes has been reviewed.

Individually indexed compounds are:

∗ 1-Acetoxy-6-oxo-cyclodecyl hydroperoxide, 3547
Allyl hydroperoxide, 1226
∗ Barium methyl hydroperoxide, 0889
∗ Bis(2-hydroperoxy-2-butyl) peroxide, 3078
∗ Bis(2-hydroperoxy-4-methyl-2-pentyl) peroxide, 3566
1,2- or 1,4-Bis(2-hydroperoxy-2-propyl)benzene, 3542
∗ α-(4-Bromophenylazo)benzyl hydroperoxide, 3606
∗ α-(4-Bromophenylazo)phenylethyl α-hydroperoxide, 3648
∗ 2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3156
tert-Butyl hydroperoxide, 1698
2-(4-Chlorophenyl)-1,1-dimethylethyl hydroperoxide, 3018
2-Cyclohexenyl hydroperoxide, 2435
1,1-Dichloroethyl hydroperoxide, 0794
3,5-Dimethyl-3-hexyl hydroperoxide, 3075
Ethyl hydroperoxide, 0925
1-Hydroperoxphenylethane, 2985
Isopropyl hydroperoxide, 1283
Methyl hydroperoxide, 0486
∗ α-Phenylazobenzyl hydroperoxide, 3609
∗ α-Phenylazo-4-bromobenzyl hydroperoxide, 3607
∗ α-Phenylazo-4-fluorobenzyl hydroperoxide, 3608
2-Phenyl-1,1-dimethylethyl hydroperoxide, 3332
2-Phenyl-2-propyl hydroperoxide, 3166
2-Tetrahydrofuryl hydroperoxide, 1624
∗ 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide, 3312

See also ALLYLIC HYDROPEROXIDES, α-PHENYLAZO HYDROPEROXIDES

ALKYLIMINIOFORMATE CHLORIDES

'IMINOESTER HYDROCHLORIDES' $RC(:N^+H_2)OR'\ Cl^-$

Preparative hazard

See Hydrogen chloride: Alcohols, etc.

ALKYLMETAL HALIDES **RMX, RMX_2, R_2MX**

This highly reactive group of organometallic compounds includes the groups:

ALKYLALUMINIUM HALIDES, GRIGNARD REAGENTS, TRIALKYLANTIMONY HALIDES

and the individually indexed compounds:

∗ Bis(chloromethyl)thallium chloride, 0796
∗ Chloroethylbismuthine, 0892
∗ Dichlorodi-μ-chlorobis(pentamethylcyclopentadienyl)dirhodium, 3806
Diethylbismuth chloride, 1676
Diethylgold bromide, 1672
Dimethylantimony chloride, 0900
Dimethylbismuth chloride, 0893
Ethylmagnesium iodide, 0859
Methylmagnesium iodide, 0446
Methylzinc iodide, 0447

ALKYLMETAL HYDRIDES **R_mMH_n**

This small group shows high reactivity or instability, individual compounds being:

Diethylgallium hydride, 1721
Methylstibine, 0499
∗ Chloroethylbismuthine, 0892

ALKYLMETALS

This reactive and usually pyrophoric class includes the groups

DIALKYLMAGNESIUMS, DIALKYLZINCS, DIPLUMBANES, TRIALKYLALUMINIUMS, TRIALKYLBISMUTHS

DropBooks

and the individually indexed compounds:

∗ Acetylenebis(triethyllead), 3672
∗ Acetylenebis(triethyltin), 3674
Allyllithium, 1177
∗ Benzylsodium, 2787
∗ Bis(1-chloroethylthallium chloride) oxide, 1591
∗ Bis(dimethylamino)dimethylstannane, 2597
∗ Bis(dimethylstibinyl) oxide, 1761
∗ Bis(dimethylthallium)acetylide, 2519
∗ Bis(trifluoromethyl)cadmium-1,2-dimethoxyethane adduct, 0587
∗ Bis(trimethylsilylmethyl)magnesium, 3099
3-Buten-1-ynyltriethyllead, 3357
∗ 1-Butoxyethyl 3-trimethylplumbylpropiolate, 3552
Butyllithium, 1651
tert-Butyllithium, 1652
Butylsodium, 1667
∗ 2-Chlorovinyltrimethyllead, 1989

Cyclopentadienylgold(I), 1839
Cyclopentadienylsodium, 1855
μ-Cyclopentadienyltrimethyltitanium, 3038
* 1,2-Diaminoethanebis(trimethylgold), 3105
* Di-2-butenylcadmium, 3027
Dibutylmagnesium, 3068
* Dibutylthallium isocyanate, 3193
Dibutylzinc, 3080
Diethylberyllium, 1675
Diethylcadmium, 1677
* Diethyllead dinitrate, 1692
Diethylmagnesium, 1687
Diethyl telluride, 1717
Diethylzinc, 1718
Diisobutylzinc, 3081
Diisopentylmercury, 3368
Diisopentylzinc, 3371
Diisopropylberyllium, 2535
Dimethylberyllium, 0890
* Dimethylberyllium-1,2-dimethoxyethane, 0891
Dimethylcadmium, 0894
* Di-μ-methylenebis(methylpentamethylcyclopentadienyl)dirhodium, 3855
Dimethylmagnesium, 0908
Dimethylmanganese, 0909
Dimethylmercury, 0907
Dimethyl(phenylethynyl)thallium, 3298
Dimethyl-1-propynylthallium, 1938
* (Dimethylsilylmethyl)trimethyllead, 2605
* Dimethyltin dinitrate, 0914
Dimethylzinc, 0935
Dipropylmercury, 2537
* Divinylmagnesium, 1498
* Divinylzinc, 1547
* Dodecamethyltetraplatinum(IV) perchlorate, 3587
* 3-Ethoxycarbonyl-4,4,5,5-tetracyano-3-trimethylplumbyl-4,5-dihydro-3*H*-pyrazole, 3611
* Ethylenedicaesium, 0798
Ethyllithium, 0862
Ethylsodium, 0877
μ,1,1′-Ferrocenediyldilithium, 3256
* Hexacyclohexyldilead, 3894
Hexamethyldiplatinum, 2606
* Hexamethylerbium–hexamethylethylenediaminelithium complex, 2592
Hexamethylrhenium, 2607
Hexamethyltungsten, 2609
* Lithium hexamethylchromate(3−), 2590

∗ Lithium pentamethyltitanate−bis(2,2′-bipyridine), 2042
∗ Lithium tetramethylchromate(II), 1744
∗ Methylaluminiumbis(pentamethylcyclopentadienyltrimethyliridium), 3866
∗ Methylbismuth oxide, 0428
3-Methyl-3-buten-1-ynyltriethyllead, 3413
Methylcopper, 0440
Methylenedilithium, 0401
Methylenemagnesium, 0402
Methyllithium, 0452
Methylpotassium, 0448
Methylsilver, 0421
Methylsodium, 0463
Octylsodium, 3053
Pentamethyltantalum, 2046
Potassium cyclopentadienide, 1846
Propylcopper(I), 1251
Propyllithium, 1253
Propylsodium, 1269
∗ Tellurane-1,1-dioxide, 1980
∗ Tetraallyluranium, 3548
Tetraethyllead, 3095
Tetraethyltin, 3097
Tetraisopropylchromium, 3577
∗ Tetramethylbis(trimethysilanoxy)digold, 3382
Tetramethyldigallane, 1748
Tetramethyldistibane, 1769
Tetramethyllead, 1767
Tetramethylplatinum, 1768
Tetramethyltellurium(IV), 1772
† Tetramethyltin, 1771
∗ Tetravinyllead, 3016
∗ Triallylchromium, 3180
Tributylgallium, 3572
Tributylindium, 3573
∗ Tributyl(phenylethynyl)lead, 3811
† Triethylaluminium, 2553
Triethylantimony, 2574
Triethylgallium, 2563
Triethylindium, 2564
Trimethylaluminium, 1291
Trimethylantimony, 1320
Trimethylbismuthine, 1298
Trimethylgallium, 1305
∗ Trimethylgermylphosphine, 1332
Trimethylindium, 1307

DropBooks

∗ Trimethylsilylmethyllithium, 1722
Trimethylthallium, 1321
Tripropylantimony, 3221
Tripropylindium, 3219
∗ Tripropyllead fulminate, 3363
Tris(trimethylsilyl)aluminium etherate, 3620
∗ Tris(trimethylsilylmethyl)aluminium, 3584
∗ Tris(trimethylsilylmethyl)indium, 3585
∗ Trivinylantimony, 2405
∗ Trivinylbismuth, 2391
∗ Vinyllithium, 0757

See also ARYLMETALS, METAL ACETYLIDES

See LITHIUM PERALKYLURANATES, TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES, ALKYLALUMINIUM DERIVATIVES

See ARYLMETALS

ALKYL NITRATES $RONO_2$

Alone, or Lewis acids

1. Boschan, R. *et al.*, *Chem. Rev.*, 1955, **55**, 505
2. Slavinskaya, R. A., *J. Gen. Chem. (USSR)*, 1957, **27**, 844
3. Boschan, R. *et al.*, *J. Org. Chem.*, 1960, **25**, 2012
4. Smith, 1966, Vol. 2, 458
5. Rüst, 1948, 284
6. Urbanski, 1965, Vol. 2, 128
7. Marker, C. D. *et al.*, *Synthesis*, 1977, 485–486
8. Olah, G. A. *et al.*, *Synthesis*, 1978, 452–453
9. Dougherty, V., *J. Haz. Mat.*, 1983, **7**, 247–258
10. Colclough, M. E. *et al.*, *Polym. Adv. Technol.*, 1994, **5**(9), 554

The group of potentially or actually explosive compounds has been reviewed [1]. Ethyl [1], isopropyl, butyl, benzyl and triphenylmethyl nitrates [3] in contact with sulfuric acid [2], tin(IV) chloride [2,3] or boron trifluoride [3] interact violently (after an induction period of up to several hours) with gas evolution. An autocatalytic mechanism was proposed. Although pure alkyl nitrates are stable in storage, traces of oxides of nitrogen sensitise them to decomposition, and may cause explosion on heating or storage at ambient temperature [4].

The most important applications of alkyl nitrates are based on their explosive properties. Methyl and ethyl nitrates are too volatile for widespread use; propyl nitrate has been used as a liquid monopropellant (as also has isopropyl nitrate). Ethylene dinitrate, glyceryl trinitrate and pentaerythritol tetranitrate are widely used as explosives, the two former liquids adsorbed on or blended with other compounds [1]. Poly(nitrate esters) such as poly(glycidyl nitrate) are being studied as energetic binders for explosives and propellants [10]. The nitrate esters of many polyhydroxy compounds (ethylene glycol, glycerol, 1-chloro-2,3-dihydroxypropane, erythritol, mannitol, sugars or cellulose) are all more or less shock-sensitive and will ignite or

explode on heating [5]. Glyceryl dinitrate is a slightly less sensitive and powerful explosive than the trinitrate, while the mononitrate explodes at 170°C in a sealed tube [6]. Use of dichloromethane as diluent provides a low-hazard procedure for preparing such esters [7], and in a new method of preparation, the esters are not isolated from solution in acetonitrile [8]. Methods of assessing the relative thermal stabilities of formulated propellant materials containing nitrate esters are reviewed. and a new test to measure isothermal time to auto-ignition is described, together with the Osawa method of predicting the half-life of the substances [9].

Transition metal derivatives

Lur'e, B. A. *et al., Chem. Abs.*, 1981, **95**, 83199

The decomposition rates of several glycol nitrates and glyceryl trinitrate are greatly enhanced by the presence of transition metal oxides or chelates.

The decomposition rates of several glycol nitrates and glyceryl trinitrate are greatly enhanced by the presence of transition metal oxides or chelates.

2-*trans*-1-Azido-1,2-dihydroacenaphthyl nitrate, 3466
Benzyl nitrate, 2765
2,2-Bis[(nitrooxy)methyl]propane-1,3-diol dinitrate, 1901
∗ Bis(2-nitratoethyl)nitric amide, 1602
Butyl nitrate, 1661
∗ 1-Chloro-2,3-propylene dinitrate, 1160
2-Cyano-2-propyl nitrate, 1506
∗ 2-Diethylammonioethyl nitrate nitrate, 2571
∗ 2,3-Epoxypropyl nitrate
Ethylidene dinitrate, 0811
† Ethyl nitrate, 0870
Glyceryl trinitrate, 1196
† Isopropyl nitrate, 1266
Isosorbide dinitrate, 2380
Methyl nitrate, 0457
2,2′-Oxybis(ethyl nitrate), 1599
† Propyl nitrate, 1267
Triphenylmethyl nitrate, 3782

See also Lithium azide: Alkyl nitrates, etc., *also* NITRATING AGENTS (reference 3)
See related ALKENYL NITRATES

DropBooks

ALKYL NITRITES **RON:O**

1. Sorbe, 1968, 146
2. Rüst, 1948, 285
3. Anon., private comm., 1985

Many alkyl nitrites are thermally unstable and may readily decompose or explode on heating [1]. Methyl nitrite explodes more violently than ethyl nitrite [2]. Lower alkyl nitrites have been known to decompose and burst the container, even in refrigerated storage [3]. Individually indexed compounds are:

† Butyl nitrite, 1658
† *tert*-Butyl nitrite, 1659

Decyl nitrite, 3364
† Ethyl nitrite, 0867
† Isopentyl nitrite, 1996
† Isopropyl nitrite, 1262
† Methyl nitrite, 0455
† Pentyl nitrite, 1998
† Propyl nitrite, 1265

ALKYLNON-METAL HALIDES **REX_2, R_2EX, R_2EHX etc.**

This class of flammable, air-sensitive and usually pyrophoric compounds includes the groups:
See also ALKYLHALOBORANES, ALKYLHALOPHOSPHINES, ALKYLHALOSILANES

and the individually indexed compounds:
∗ Bis(trifluoromethyl)sulfur difluoride, 0648
Chlorodimethylarsine, 0884
∗ Cyanodimethylarsine, 1199
Dichloromethylarsine, 0424
Dimethylfluoroarsine, 0885
Dimethyliodoarsine, 0886
Ethyliodomethylarsine, 1272
Trifluoromethylsulfur trifluoride, 0363

ALKYLNON-METAL HYDRIDES **REH_2, R_2EH, R_2EH_2, R_3EH**

Several of the partially lower-alkylated derivatives of non-metal hydrides are pyrophoric in air. With other gaseous oxidants (halogens, etc.) the reaction may be explosive. The class includes the groups:
See also ALKYLBORANES, ALKYLPHOSPHINES, ALKYLSILANES

and the individually indexed compounds:
Diethylarsine, 1720
Dimethylarsine, 0937
Ethylmethylarsine, 1293
Methanetellurol, 0490
† Methanethiol, 0489
See ALKANETHIOLS, ORGANIC BASES
See also the fully alkylated class ALKYLNON-METALS, below

ALKYLNON-METALS **R_nE**

Several of the fully lower-alkylated non-metals are pyrophoric in air, and with other gaseous oxidants (halogens, etc.), reaction may be explosive. The class includes the groups:
ALKYLBORANES, ALKYLPHOSPHINES,
ALKYLSILANES, SILYLHYDRAZINES

and the individually indexed compounds:

∗ Acetyldimethylarsine, 1628
∗ Allyldimethylarsine, 1983
∗ Bis(dimethylarsinyldiazomethyl)mercury, 2467
∗ Bis(dimethylarsinyl) oxide, 1737
∗ Bis(dimethylarsinyl) sulfide, 1738
∗ Bis(trifluoromethyl) disulfide, 0644
Bis(trifluoromethyl) sulfide, 0643
∗ Dimethylphenylarsine, 2991
∗ Hexaphenylhexaarsane, 3891
∗ Lithium tetramethylborate, 1740
Tetraethyldiarsane, 3087
Tetramethyldiarsane, 1736
Tribenzylarsine, 3822
Triethylarsine, 2557
Trimethylarsine, 1294

See related TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES
See also the partially alkylated class ALKYLNON-METAL HYDRIDES

ALKYL PERCHLORATES $ROClO_3$

1. Hofmann, K. A. *et al., Ber.*, 1909, **42**, 4390
2. Meyer, J. *et al., Z. Anorg. Chem.*, 1936, **228**, 341
3. Schumacher, 1960, 214
4. Burton, H. *et al., Analyst*, 1955, **80**, 4
5. Hoffman, D. M., *J. Org. Chem.*, 1971, **36**, 1716
6. Zefirov, N. S. *et al., J. Org. Chem.*, 1985, **50**, 1875

DropBooks

Methyl, ethyl and propyl perchlorates, readily formed from the alcohol and anhydrous perchloric acid, are highly explosive oils, sensitive to shock, heat and friction [1]. Many of the explosions which have occurred on contact of hydroxylic compounds with conc. perchloric acid or anhydrous metal perchlorates are attributable to the formation and decomposition of perchlorate esters [2,3,4]. Safe procedures for preparation of solutions of 14 *sec*-alkyl perchlorates are described. Heated evaporation of solvent caused explosions in all cases [5]. 1-Chloro-2-propyl, *trans*-2-chlorocyclohexyl, 1-chloro-2-propyl, 1,6-hexanediyl, hexyl, and 2-propyl perchlorates, prepared by a new method, are all explosive oils [6].

Relevant Individual entries are:

∗ 2-Azatricyclo[2.2.1.$0^{2,6}$]hept-7-yl perchlorate, 2368
Chlorine, : 2-Chloroalkyl aryl sulfides, Lithium perchlorate, 4020
trans-2-Chlorocyclohexyl perchlorate, 2420
3-Chloro-2-hydroxypropyl perchlorate, 1207
1-Chloro-2-propyl perchlorate, 1206
Ethylene diperchlorate, 0795
Ethyl perchlorate, 0852
1,6-Hexanediyl perchlorate, 2470

Hexyl perchlorate, 2520
2(2-Hydroxyethoxy)ethyl perchlorate, 1643
Magnesium perchlorate, : Trimethyl phosphite, 1315
Methoxycarbonylmethyl perchlorate, 1166
Methyl perchlorate, 0436
* Peroxyacetyl perchlorate, 0737
Propyl perchlorate, 1249
2-Propyl perchlorate, 1250
Trichloromethyl perchlorate, 0334
Trifluoromethyl perchlorate, 0321

ALKYLPHOSPHINES **RPH_2, R_2PH, R_3P**

Many of the lower-alkyl substituted phosphines are pyrophoric; individually indexed compounds are:

* 1,2-Bis(*tert*-butylphosphino)ethane, 3378
* 1,2-Bis(di-*tert*-butylphosphino)ethane, 3776
1,2-Bis(diethylphosphino)ethane, 3379
* 1,2-Bis-(di-2-propylphosphino)ethane, 3673
* Bis(2-hydroxyethyl)methylphosphine, 2035
* Bis(trimethylphosphine)di(3,5-dibromo-2,6-dimethoxyphenyl)nickel, 3837
* Bis(trimethylphosphine)nickel(0)−acetylene complex, 3093
* Di[bis(trifluoromethyl)phosphido]mercury, 1375
* Diethyl ethanephosphonite, 2572
Diethylmethylphosphine, 2036
Diethylphosphine, 1734
* 2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclooctane, 2548
Dimethylphenylphosphine, 3003
* Dimethylphenylphosphine oxide, 3002
Dimethylphosphine, 0948
* Dimethyltrimethylsilylphosphine, 2045
* Diphenylphosphine, 3508
1,2-Diphosphinoethane, 0957
* Ethoxytriethyldiphosphinyl oxide, 3094
Ethyldimethylphosphine, 1735
Ethylenebis(dimethylphosphine), 2585
Ethylphosphine, 0949
* 5-Methyl-1(1-methylethyl)-1,2,3-azadiphosphole, 2455
Methylphosphine, 0498
* Phenylphosphine, 2360
* Potassium dinitrogentris(trimethylphosphine)cobaltate(1−), 3228
* 2-Tetrahydrofuranylidene(dimethylphenylphosphine-trimethylphosphine)-2,4,6-trimethylphenylnickel perchlorate, 3854
* 2-Tetrahydropyranylidene-bis(dimethylphenylphosphine)-3,4,6-trimethyl-phenyl-nickel perchlorate, 3877
* Tetrakis(diethylphosphino)silane, 3733

Tetramethyldiphosphane, 1765
∗ Tetramethyldiphosphane disulfide, 1766
† Tributylphosphine, 3575
Triethylphosphine, 2573
∗ Triethylphosphinegold nitrate, 2558
∗ Triethynylphosphine, 2124
Trifluoromethylphosphine, 0399
Triisopropylphosphine, 3220
Trimethylphosphine, 1319
1-Trimethylsilyloxy-1-trimethylsilylphosphylidine-2,2-dimethylpropane, 3417
∗ Triphenylphosphine, 3756
∗ Tris(2,2-dimethylethyl)triphosphirane, 3576
∗ Tris(2-propylthio)phosphine,
∗ Tris(trifluoromethyl)phosphine, 1063
See other ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

ALKYLSILANES **$RSiH_3$, R_2SiH_2, R_3SiH, R_4Si**

Griffiths, S. T. *et al.*, *Combust. Flame*, 1958, **2**, 244–252
Measurements of the autoignition temperatures for several series of mono-, di-, tri- and tetra-alkylsilanes showed that the ease of oxidation decreases with increasing substitution. In this group of easily ignited or pyrophoric compounds, individually indexed compounds are:
∗ Benzylsilane, 2832
Bis(2-fluoro-2,2-dinitroethoxy)dimethylsilane, 2421
∗ 1,2-Bis(triethylsilyl)hydrazine, 3583
∗ 1,2-Bis(triethylsilyl)trimethylsilylhydrazine, 3696
∗ *N,N′*-Bis(trimethylsilyl)aminoborane, 2612
∗ *cis*-Bis(trimethylsilylamino)tellurium tetrafluoride, 2615
∗ Bis(trimethylsilyl) chromate, 2591
∗ Bis(trimethylsilyl)mercury, 2593
∗ Bis(trimethylsilylmethyl)magnesium, 3099
† Bis(trimethylsilyl) oxide, 2601
∗ 1,2-Bis(tripropylsilyl)hydrazine, 3777
∗ *N*-*tert*-Butyl-*N*-trimethylsilylaminoborane, 2878
∗ *N*, *N′*-Di-*tert*-butyl-*N,N′*-bis(trimethylsilyl)diaminophosphene, 3675
† Diethoxydimethylsilane, 2582
† Dimethylaminotrimethylsilane, 2043
∗ (Dimethylsilylmethyl)trimethyllead, 2605
∗ Dimethyltrimethylsilylphosphine, 2045
Formyl(triisopropyl)silane, 3370
Hexamethyldisilane, 2608
† Hexamethyldisilazane, 2610
Methylsilane, 0510
Propylsilane, 1331
∗ Tetrakis(diethylphosphino)silane, 3733

DropBooks

Tetrakis(trimethylsilyl)diaminodiphosphene, 3588
∗ Tetramethyldisiloxane, 1783
† Tetramethylsilane, 1770
∗ 1,1,3,3-Tetramethylsiloxalane, 1774
∗ Triethoxysilane, 2584
Triethylsilane, 2585
∗ Triethylsilyl-1,2-bis(trimethylsilyl)hydrazine, 3586
∗ Trimethylsilylmethyllithium, 1722
∗ *N*-Trimethylsilyl-*N*-trimethylsilyloxyacetoacetamide, 3375
∗ Tris(2-pylthio)silane, 3222
∗ Tris(trimethylsilyl)aluminium, 3227
∗ Tris(trimethylsilyl)aluminium etherate, 3620
∗ *N*, *N*, *N*′-Tris(trimethylsilyl)diaminophosphine, 3232
∗ Tris(trimethylsilylmethyl)aluminium, 3584
∗ Tris(trimethylsilylmethyl)indium, 3585
∗ Tris(trimethylsilyl)phosphine, 3229
Tris(trimethylsilyl)silane, 3231
See other ALKYLNON-METAL HYDRIDES, ALKYLNON-METALS

ALKYL TRIALKYLLEAD PEROXIDES ROOPbR′$_3$

Houben-Weyl, 1975, Vol. 13.3, 111
These unstable compounds may decompose very violently on heating.
See other ORGANOMINERAL PEROXIDES

ALKYNES R−C≡C−

Oxides of Nitrogen
See Nitrogen oxide: Dienes, etc.
† Acetylene, 0686
† 1,3-Butadiyne, 1385
∗ 4,4′-(Butadiyne-1,4-diyl)bis(2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl), 3838
† Buten-3-yne, 1423
† 1-Butyne, 1481
† 2-Butyne, 1482
1,7,13-Cyclooctadecatriene-3,5,9,11,15,17-hexayne, 3740
1,7,13,19-Cyclotetracosatetraene-3,5,9,11,15,17,21,23-octayne, 3843
1,4-Diethynylbenzene, 3241
11,12-Diethynyl-9,10-dihydro-9,10-ethenoanthracene, 3792
3,3-Dimethyl-1-butyne, 2408
1,8-Diphenyloctatetrayne, 3788
Hepta-1,3,5-triyne, 2641
1-Heptene-4,6-diyne, 2707
† 1-Heptyne, 2838
1,3-Hexadien-5-yne, 2290

† 1,5-Hexadien-3-yne, 2291
1,5-Hexadiyne, 2292
2,4-Hexadiyne, 2293
1,3,5-Hexatriyne, 2074
3-Hexyne, 2415
† 1-Hexyne, 2414
† 2-Methyl-1-buten-3-yne, 1858
† 3-Methyl-1-butyne, 1894
3-Nitrophenylacetylene, 2905
∗ 1,3,7-Octatrien-5-yne, 2944
† 1-Octyne, 3022
† 2-Octyne, 3023
† 3-Octyne, 3024
† 4-Octyne, 3025
† 1-Pentyne, 1898
† 2-Pentyne, 1899
Phenylacetylene, 2912
∗ Poly(butadiyne), 1386
† Propyne, 1125

See other ACETYLENIC COMPOUNDS

See ACYL AZIDES

See also ROTANES

ALLOYS

INTERMETALLIC COMPOUNDS

DropBooks

Individually indexed alloys or intermetallic compounds are:
Aluminium amalgam, 0051
Aluminium–copper–zinc alloy, 0050
Aluminium–lanthanum–nickel alloy, 0080
Aluminium–lithium alloy, 0052
Aluminium–magnesium alloy, 0053
Aluminium–nickel alloys, 0055
Aluminium–titanium alloys, 0056
Copper–zinc alloys, 4268
Ferromanganese, 4389
Ferrotitanium, 4391
Lanthanum–nickel alloy, 4678
Lead–tin alloys, 4883
Lead–zirconium alloys, 4884
Lithium–magnesium alloy, 4681
Lithium–tin alloys, 4682
Plutonium bismuthide, 0231
Potassium antimonide, 4673
Potassium–sodium alloy, 4646
Silicon–zirconium alloys, 4910

Silver–aluminium alloy, 0002
∗ Silvered copper, 0003
Sodium–antimony alloy, 4797
Sodium germanide, 4418
Sodium–zinc alloy, 4798
Titanium–zirconium alloys, 4921
See also LANTHANIDE–TRANSITION METAL ALLOY HYDRIDES

ALLYL COMPOUNDS $H_2C{=}CHCH_2-$

Several allyl compounds are notable for their high flammability and reactivity. There are group entries for:
See also ALLYLIC HYDROPEROXIDES, ALLYL TRIFLUOROMETHANESULFONATES

Individually indexed compounds are:
† Allyl acetate, 1912
Allyl benzenesulfonate, 3155
∗ Allyldimethylarsine, 1983
† Allyl formate, 1524
Allyl hydroperoxide, 1226
∗ Allyl isothiocyanate, 1471
Allyllithium, 1177
Allylmercury(II) iodide, 1173
1-Allyloxy-2,3-epoxypropane, 2434
Allyl phosphorodichloridite, 1169
N-Allylthiourea, 1600
Allyl 4-toluenesulfonate, 3315
† Allyl vinyl ether, 1904
† 3-Aminopropene, 1254
3-Azidopropene, 1188
† 1-Bromo-2-butene, 1548
† 3-Bromo-1-propene, 1153
N-Chloroallylamine, 1202
1-Chloro-4-(2-nitrophenyl)-2-butene, 3270
† 3-Chloropropene, 1158
† 3-Cyanopropene, 1465
† Diallylamine, 2450
† Diallyl ether, 2431
Diallyl peroxydicarbonate, 2989
Diallyl phosphite, 2456
Diallyl sulfate, 2443
Diallyl sulfide, 2447
∗ Di-2-butenylcadmium, 3027
† 3,3-Dimethoxypropene
1-Heptene-4,6-diyne, 2707
† 3-Iodopropene, 1174

† 2-Propene-1-thiol, 1239
† 2-Propen-1-ol, 1223
Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3505
Tetraallyl-2-tetrazene, 3545
∗ Tetraallyluranium, 3548
∗ Triallylchromium, 3180
2,4,6-Triallyloxy-1,3,5-triazine, 3530
Triallyl phosphate, 3184
3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2847
See other PEROXIDISABLE COMPOUNDS

ALLYLIC HYDROPEROXIDES **−CH=CH−CH(OOH)−**

Preparative hazard
Frimer, A. A., *J. Org. Chem.*, 1977, **42**, 3194−3196, footnote 7
A new method of preparation involves interaction of allylic halides in solvents with 98% hydrogen peroxide in presence of silver ion and base at ambient temperature under argon. The reactions must be run in the dark to prevent precipitation of metallic silver, which will catalyse decomposition of the hydroperoxide or excess hydrogen peroxide. In an experiment not run in the dark, the hydroperoxide from 3-chlorocyclohexene ignited spontaneously after isolation and concentration.
See other ALKYL HYDROPEROXIDES

ALLYL TRIFLUOROMETHANESULFONATES **$RCH{=}CR'CH_2OSO_2CF_3$**

DropBooks

Alone, or Aprotic solvents
Vedejs, E. *et al.*, *J. Org. Chem.*, 1977, **42**, 3109−3113
Trifluoromethanesulfonate esters (‘triflates’) of allyl alcohol and its derivatives are very reactive and undiluted samples must be stored in vented containers at −78°C. A chilled sample of allyl triflate in a sealed ampoule exploded on being allowed to warm to ambient temperature. The esters react violently with aprotic solvents such as DMF or DMSO. Individually indexed compounds are:
2-Chloro-2-propenyl trifluoromethanesulfonate, 1426
3-Methoxycarbonylpropen-2-yl trifluoromethanesulfonate, 2353
Prop-2-enyl trifluoromethanesulfonate, 1461
3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2847
See other ALLYL COMPOUNDS, SULFUR ESTERS

AMINATION INCIDENTS

Gordon, M. D., *Adv. Instrum.*, 1988, **43**(1), 75−81
Kinetic simulation methods are used as advisory controls in potentially thermally hazardous batch amination reactions of nitroaromatic compounds. Time−temperature process data are fed as input to a kinetic simulation computer program which calculates conversions, heat release and pressure profiles. Results

are compared continuously on-line with measured batch data to detect any deviations from normal operating conditions.

Incidents involving reactions with either ammonia or organic amines (sometimes only in catalytic proportions) may be found under the entries:
Benzenediazonium-2-carboxylate, : Aniline, or Isocyanides, 2659
4-Chloroacetophenone, : Dimethylamine, 2929
1-Chloro-2,4-dinitrobenzene, : Ammonia, 2098
2-Chloronitrobenzene, : Ammonia, 2141
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

AMINE OXIDES $RR'R''N\rightarrow O$

Editor's comments
Several tertiary amine oxides are reported as exploding, usually on heating well above 100°C. Paradoxically, these tend to be the more stable members of the group, those which for conformational reasons cannot undergo the Cope rearrangement. As this class of compound is of growing importance, more incidents can be expected, possibly including violent decomposition of the alkylhydroxylamine products of the Cope reaction as well as the apparently radical branched chain, higher temperature decomposition which accounts for present reports. Early workers developed spot tests for amine oxides which later study has shown they do not perform but hydrogen peroxide does; since amine oxides tenaciously hold water as hydrates it must be suspected that they can also form hydrogen peroxidates if made using excess hydrogen peroxide. These will be more dangerous than the amine oxide itself.
See also CRYSTALLINE HYDROGEN PEROXIDATES
See other N–O COMPOUNDS, *N*-OXIDES

AMINIUM IODATES AND PERIODATES $RN^+H_3\ IO_3^-$, $RN^+H_3IO_4^-$

Fogel'zang, A. E. *et al.*, *Chem. Abs.*, 1975, **83**, 8849
Combustion rates of the periodate salts of amines exceed those of the corresponding iodate salts.
See OXOSALTS OF NITROGENOUS BASES, PERCHLORATE SALTS OF NITROGENOUS BASES

AMINIUM NITRATES $RN^+H_3\ NO_{3-}$

1. Anon., *Chem. Hazards Ind.*, 1992, (Jul.) 1218
Many nitrate salts of amines are highly crystalline, which encourages their use to isolate amines; they are also often explosive, which does not. An industrial explosion consequent upon inadvertent isolation of such in part of a production plant, with subsequent overheating is reported [1].

Nitric Acid: Alkylamines
OXOSALTS OF NITROGENOUS BASES

AMINIUM PERCHLORATES $RN^+H_3\ ClO_4^-$

Datta, R. L. *et al.*, *J. Chem. Soc.*, 1919, **115**, 1006–1010

Many perchlorate salts of amines explode in the range 215–310°C, and some on impact at ambient temperature. Individually indexed compounds are to be found in the group entries:

PERCHLORATE SALTS OF NITROGENOUS BASES
POLY(AMINIUM) PERCHLORATES

AMINOMETHOXY COMPOUNDS H_2N-Alkyl-OMe, H_2N-Aryl-OMe

Several members of this group show considerable energies of decomposition by DSC examnination.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Individually indexed compounds are:

2-Bromo-3,5-dimethoxyaniline, 2974
3-Chloro-4-methoxyaniline, 2795
3,5-Dimethoxyaniline, 2999
2-Methoxyaniline, 2816
3-Methoxyaniline, 2817
4-Methoxyaniline, 2818
∗ 2-Methoxyanilinium nitrate, 2829
3-Methoxybenzylamine, 2997
† 2-Methoxyethylamine, 1312
2-Methoxy-5-nitroaniline, 2802
4-Methoxy-1,3-phenylenediamine, 2826
∗ 1-(4-Methoxyphenyl)-3-methyltriazene, 3000
3-Methoxypropylamine, 1730

See other ORGANIC BASES

DropBooks

AMMINECHROMIUM PEROXOCOMPLEXES $H_3N \rightarrow Cr{-}OO{-}$

This group of compounds, previously described as 'amine perchromates', is characterised by the presence of basic nitrogen and peroxo ligands within the same coordination sphere. This creates a high tendency towards explosive decomposition, which sometimes apparently occurs spontaneously. Individually indexed compounds are:

Ammine-1,2-diaminoethanediperoxochromium(IV), 0968
Aqua-1,2-diaminoethanediperoxochromium(IV), 0965
Aqua-1,2-diaminopropanediperoxochromium(IV) dihydrate, 1336
Bis(2-aminoethyl)aminediperoxochromium(IV), 1776
1,2-Diamino-2-methylpropaneoxodiperoxochromium(VI), 1746
Dianilineoxodiperoxochromium(VI), 3523
∗ (Dimethyl ether)oxodiperoxochromium(VI), 0904
∗ Hexamethylenetetrammonium tetraperoxochromate(V)?, 3779
Hydrogen cyanide, 0380

Oxodiperoxodipyridinechromium(VI), 3274
* Oxodiperoxodi(pyridine *N*-oxide)molybdenum, 3279
* Oxodiperoxodi(pyridine *N*-oxide)tungsten, 3283
Oxodiperoxodiquinolinechromium(VI), 3748
* Oxodiperoxomolybdenum–hexamethylphosphoramide, 4718
Oxodiperoxopyridinechromium *N*-oxide, 1844
* Oxodiperoxy(pyridine)(1,3-dimethyl-2,4,5,6-tetrahydro-2-1*H*)-pyrimidinone) molybdenum, 3410
* μ-Peroxobis[ammine(2,2′,2″-triaminotriethylamine)cobalt(III)](4+) perchlorate, 3591
* Potassium pentacyanodiperoxochromate(5−), 1810
Triamminediperoxochromium(IV), 4231
* Triphenylphosphine oxide-oxodiperoxochromium(VI), 3752

See PEROXOCHROMIUM COMPOUNDS
See related AMMINEMETAL OXOSALTS

AMMINEMETAL AZIDES $H_3N{\rightarrow}Co{-}N_3$

1. Joyner, T. B., *Chem. Abs.*, 1970, **72**, 113377
2. Narang, K. K. *et al., Synth. React. Inorg. Met.-Org. Chem.*, 1996, **26**(4), 573

The explosive properties of a series of 5 amminecobalt(III) azides were examined in detail. Compounds were hexaamminecobalt triazide, pentaammineazidocobalt diazide, *cis*- and *trans*-tetraamminediazidocobalt azide, triamminecobalt triazide [1]. A variety of hydrazine complexed azides and chloroazides of divalent metals have been prepared. Those of iron, manganese and copper could not be isolated; cobalt, nickel, cadmium and zinc gave products stable at room temperature but more or less explosive on heating [2].

See related METAL AZIDES, METAL AZIDE HALIDES

AMMINEMETAL HALIDES $H_3N \rightarrow M^+X^-$

Author's comment.
Although free from the formally oxidising anions present in the two groups below, a few of these compounds show instability. These are:
cis-Bis(trimethylsilylamino)tellurium tetrafluoride, 2615
Pentaamminechlororuthenium chloride, 4137
N,N,N′,N′-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) bromide, 3225
N,N,N′,N′-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) iodide, 3226

See AMMINEMETAL OXOSALTS

AMMINEMETAL NITRATES $H_3N \rightarrow M^+NO_3^-$

Author's comment.
Compounds in this group show explosive instability tending towards that of the perchlorate analogues in the entry following. Individual nitrates are:

Bis(2-aminoethyl)aminesilver nitrate, 1773
Bis(1-methylbenzotriazole)cobalt(II) nitrate, 3652
Diamminenitratocobalt(II) nitrate, 4202
Diamminepalladium(II) nitrate, 4562
Hexaamminechromium(III) nitrate, 4234
∗ Hexaamminecobalt(III) hexanitrocobaltate(3−), 4219
Hexaamminecobalt(III) nitrate, 4210
∗ Hexahydroxylaminecobalt(III) nitrate, 4211
∗ Hexaureachromium(III) nitrate, 2623
Pentaamminenitratocobalt(III) nitrate, 4207
Pentaamminenitrochromium(III) nitrate, 4233
Tetraamminecopper(II) nitrate, 4276
Tetraamminehydroxynitratoplatinum(IV) nitrate, 4594
Tetraamminenickel(II) nitrate, 4587
Tetraamminepalladium(II) nitrate, 4588
Tetraammineplatinum(II) nitrate, 4589
Triamminenitratoplatinum(II) nitrate, 4582
1,2,4-Triazolo[4,3-*a*]pyridine−silver nitrate, 2270
∗ Triethylphosphinegold nitrate, 2558
Tris(2,3-diaminobutane)nickel(II) nitrate, 3589
Tris(1,2-diaminoethane)cobalt(III) nitrate, 2622

See AMMINEMETAL OXOSALTS (next below)

AMMINEMETAL OXOSALTS $H_3N \rightarrow M^+EO_n^-$

DropBooks

1. Mellor, 1941, Vol. 2, 341−364, 404
2. Tomlinson, W. R. *et al., J. Amer. Chem. Soc.*, 1949, **71**, 375
3. Wendlandt, W. W. *et al., Thermal Properties of Transition Metal* Complexes, Barking, Elsevier, 1967
4. Bretherick, L., *J. Chem. Educ.*, 1970, **47**, A204
5. Ray, P., *Chem. Rev.*, 1961, **61**, 313
6. Joyner, T. B., *Can. J. Chem.*, 1969, **47**, 2729−2730
7. Hoppesch, C. W. *et al., ACS Div. Fuel Chem. Preprints*, 1963, **7**(3), 235−241
8. Friederich, W. *et al., Chem. Abs.*, 1927, **21**, 1184
9. Anagnostopoulos, A. *et al., J. Inorg. Nucl. Chem.*, 1974, **36**, 2235−2238
10. Patil, K. C., *Thermochim. Acta*, 1976, **15**, 257−260
11. Springborg, J. *et al., Inorg. Synth.*, 1978, **18**, 78
12. Shidlovskii, A. A. *et al., Chem. Abs.*, 1979, **90**, 57447
13. Robinson, W. R., *J. Chem. Educ.*, 1985, **62**(11), 1001
14. Hasenpusch, W. J., *Prakt Chem./Chem. Ztg.*, 1993, **335**(2), 193

Metal compounds containing both coordinated ammonia, hydrazine, hydroxylamine or similar nitrogenous donors, and coordinated or ionic perchlorate, chlorate, nitrate, nitrite, nitro, permanganate or other oxidising groups will decompose violently under various conditions of impact, friction or heat [1,2]. From tabulated data for 17 such compounds of Co and Cr, it is considered that oxygenated *N*-coordinated compounds, (particularly those which are oxygen balanced) cover

a wide range of explosive types; many may explode powerfully with little or no provocation, and should be considered extremely dangerous, as some are sensitive enough to propagate explosion under water. The same considerations may be expected to apply to ammines of silver, gold, cadmium, lead and zinc which contain oxidising radicals [2]. The topic has been reviewed [3] and possible hazards in published student preparations were emphasised [4]. Some of the derivatives of metal biguanide and guanylurea complexes [5] are of this group.

Unexpected uniformities observed in the impact-sensitivities of a group of 22 amminecobalt oxosalts are related to kinetic factors during the initiation process [6]. A series of ammine derivatives of cadmium, cobalt, copper, mercury, nickel, platinum and zinc with (mainly) iodate anions was prepared and evaluated as explosives [7]. Earlier, ammine and hydrazine derivatives of cadmium, cobalt, copper and nickel with chlorate or perchlorate anions had been evaluated as detonators. Dihydrazinecopper(II) chlorate had exploded when dried at ambient temperature [8].

A series of pyrazole complexes which decompose explosively above 200°C is notable in that the anion is sulfate, rather than the more obvious oxidant species usually present. The compounds are manganese sulfate complexed with 4 mol of pyrazole or 3-methylpyrazole, and cadmium or zinc sulfates complexed with 4 and 3 mol of 3-methylpyrazole, respectively [9]. Around 100°C the hexaammine diperchlorates of copper and zinc decompose to the tetraammines, and those of cadmium, cobalt, manganese and nickel to the diammines. Around 220°C all these lower ammines decompose explosively to the metal oxides (or the chloride for cadmium) [10]. The use of a soft polythene rod is recommended to reduce the possibility of explosions when handling perchlorate and similar salts on sintered filters [11]. Ignition temperatures and burning velocities of the hydrazine complexes of the picrates, styphnates or nitrates of cobalt, copper or nickel were 100°C lower, and an order of magnitude higher, respectively, than those of the corresponding ammine complexes [12]. A 3 g sample of the perchlorate salt of a polyaminerhodium complex exploded with great violence in a rotary evaporator flask heated in a water bath [13]. A series of tetrammine metal(II) nitrates (Pt, Pd, Cu, Ni) were all found to be practically and legally classifiable as sensitive explosives. It was sugggested that heavy metal contamination was responsible for the ammonium nitrate/sulphate explosion at Oppau [14].

Individually indexed compounds in this large group are:

Ammonium hexanitrocobaltate(3−), 4206

Aquafluorobis(1,10-phenanthroline)chromium(III) perchlorate, 3846

∗ Basic trihydrazinecadmium perchlorate, 3951

(Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2614

∗ 2,2′-Bipyridine *N,N′*-dioxide-dicarbonylrhodium(I) perchlorate, 3454

4,4′-Bipyridyl-bis(pentaammineruthenium(III) perchlorate), 3385

2,2′-Bipyridyldichloropalladium(IV) perchlorate, 3255

Bis(2-aminoethyl)aminesilver nitrate, 1773

N,N′-Bis(3-aminopropyl)-1,4-diazacycloheptanenickel(II) perchlorate, 3415

Bis(1,2-diaminoethane)diaquacobalt(III) perchlorate, 1793
Bis(1,2-diaminoethane)dichlorocobalt(III) chlorate, 1786
Bis(1,2-diaminoethane)dichlorocobalt(III) perchlorate, 1787
cis-Bis(1,2-diaminoethane)dinitrocobalt(III) iodate, 1784
Bis(1,2-diaminoethane)dinitrocobalt(III) perchlorate, 1784
Bis(1,2-diaminoethane)hydroxooxorhenium(V) perchlorate, 1791
Bis(1,2-diaminopropane)-*cis*-dichlorochromium(III) perchlorate, 2613
Bis(diethylenetriamine)cobalt(III) perchlorate, 3106
∗ 1,2-Bis(diphenylphosphino)ethanepalladium(II) perchlorate, 3864
Bis(hydrazine)diperchloratochromium(III) perchlorate, 4128
Bis(hydrazine)nickel perchlorate, 4069
∗ Bis(hydrazine)tin(II) chloride, 4070
∗ Bis(hydroxylamine)zinc chloride, 4067
∗ Bis(2-methyl-1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3833
∗ Bis(1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3791
∗ Bis *O,N*[(*N*′-pent-2-en-2-oxy-4-ylidene)-*N,S*-dimethyldithiocarbazate] copper(II)perchlorate, 3718
Bis(*O*-salicylidenaminopropylaziridine)iron(III) perchlorate, 3853
∗ Bis(tetramethyldiphosphane disulfide)cadmium perchlorate, 3102
∗ Carbonyl-bis(triphenylphosphine)iridium−silver diperchlorate, 3898
∗ 5-*p*-Chlorophenyl-2,2-dimethyl-3-hexanone, 3664
Copper(II) perchlorate, : Polyfunctional amines, 4057
Copper(II) perchlorate, : *N*-(2-Pyridyl)acylacetamides, 4057
2(5-Cyanotetrazole)pentaamminecobalt(III) perchlorate, 0974
∗ 1,5-Cyclooctadiene-bis(4-chloropyridine *N*-oxide)rhodium(I) perchlorate, 3761
Diamminenitratocobalt(II) nitrate, 4202
Diamminepalladium(II) nitrate, 4562
Diamminepalladium(II) nitrite, 4559
cis-Diammineplatinum(II) nitrite, 4560
Diamminesilver permanganate, 0018
trans-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) perchlorate, 3376
∗ Dicarbonyl(phenanthroline *N*-oxide)rhodium(I) perchlorate, 3626
∗ Dicarbonylpyrazinerhodium(I) perchlorate, 2147
∗ *trans*-Dichlorobis[1,2-phenylenebis(dimethylarsine)]palladium(IV) diperchlorate, 3808
∗ Di[*N,N*′-Ethylenebis(2-oxidoacetophenoneiminato)copper(II)] oxovanadium(IV) diperchlorate, 3893
Dihydrazinecobalt(II) chlorate, 4049
Dihydrazinemanganese(II) nitrate, 4570
Dihydrazinesilver nitrate, 0019
6,6′-Dihydrazino-2,2′-bipyridylnickel(II) perchlorate, 3303
Dipyridinesilver(I) perchlorate, 3267
∗ Di[tris(1,2-diaminoethanechromium(III)] triperoxodisulfate, 3592
∗ Di[tris-1,2-diaminoethanecobalt(III)] triperoxodisulfate, 3593

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Hexaamminechromium(III) nitrate, 4234
Hexaamminechromium(III) perchlorate, 4129
Hexaamminecobalt(III) chlorate, 4125
Hexaamminecobalt(III) hexanitrocobaltate(3−), 4219
Hexaamminecobalt(III) iodate, 4208
Hexaamminecobalt(III) nitrate, 4210
Hexaamminecobalt(III) perchlorate, 4126
Hexaamminecobalt(III) permanganate, 4209
Hexaamminenickel chlorate, 4074
Hexaamminenickel perchlorate, 4075
Hexahydroxylaminecobalt(III) nitrate, 4211
∗ Hexakis(pyridine)iron(II) tridecacarbonyltetraferrate(2−), 3906
∗ Hexamethylenetetrammonium tetraperoxochromate(V)?, 3779
∗ Hexaureachromium(III) nitrate, 2623
∗ Hexaureagallium(III) perchlorate, 2620
4-[2-(4-Hydrazino-1-phthalazinyl)hydrazino]-4-methyl-2-pentanone(4-hydrazino-1-phthalazinyl)hydrazonedinickel(II) tetraperchlorate, 3836
Isonicotinamidepentaammineruthenium(II) perchlorate, 2618
∗ Mercury(II) perchlorate, 4078
Octammine-μ-hydroxy[μ-(peroxy-*O*:*O'*)]dirhodium(3+) perchlorate, 4138
Octaammine-μ-hydroxy[-μ-(superoxido-*O*,*O'*)]dirhodium(4+) nitrate, 4597
∗ Oxybis(*N*,*N*-dimethylacetamidetriphenylstibonium) perchlorate, 3911
Pentaammineaquacobalt(III) chlorate, 4124
Pentaamminechlorocobalt(III) perchlorate, 4123
Pentaamminedinitrogenosmium(II) perchlorate, 4072
Pentaamminenitratocobalt(III) nitrate, 4207
Pentaamminenitrochromium(III) nitrate, 4233
Pentaamminephosphinatochromium(III) perchlorate, 4053
Pentaamminephosphinatocobalt(III) perchlorate, 4050
Pentaamminepyrazineruthenium(II) perchlorate, 1792
Pentaamminepyridineruthenium(II) perchlorate, 2048
Pentaamminethiocyanatocobalt(III) perchlorate, 0519
Pentaamminethiocyanatoruthenium(III) perchlorate, 0520
∗ Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3778
∗ μ-Peroxobis[ammine(2,2′,2″-triaminotriethylamine)cobalt(III)](4+) perchlorate, 3591
∗ Tetraacrylonitrilecopper(I) perchlorate, 3510
∗ Tetra(3-aminopropanethiolato)trimercury perchlorate, 3582
Tetraamminebis(dinitrogen)osmium(II) perchlorate, 4071
Tetraammine-2,3-butanediimineruthenium(III) perchlorate, 1794
Tetraamminecadmium permanganate, 3956
Tetraamminecopper(II) bromate, 0264
Tetraamminecopper(II) nitrate, 4276
Tetraamminecopper(II) nitrite, 4275
Tetraamminecopper(II) sulfate, 4274
Tetraamminedithiocyanatocobalt(III) perchlorate, 0969

Tetraamminehydroxynitratoplatinum(IV) nitrate, 4594
Tetraamminepalladium(II) nitrate, 4588
Tetraamminezinc peroxodisulfate, 4586
1,4,8,11-Tetraazacyclotetradecanenickel(II) perchlorate, 3376
Tetrakis(μ_3-2-amino-2-methylpropanolato)tetrakis(μ_2-2.amino-2-methylpropanolato)hexacopper(II) perchlorate, 3883
Tetrakis(3-methylpyrazole)cadmium sulfate, 3716
Tetrakis(3-methylpyrazole)manganese(II) sulfate, 3717
Tetrakis(4-*N*-methylpyridinio)porphinecobalt(III)(5+) perchlorate, 3908
Tetrakis(4-*N*-methylpyridinio)porphineiron(III)(5+) perchlorate, 3909
Tetrakis(pyrazole)manganese(II) sulfate, 3538
∗ Tetrakis(thiourea)manganese(II) perchlorate, 1785
Triamminenitratoplatinum(II) nitrate, 4582
Triamminetrinitrocobalt(III), 4204
∗ 1,4,7-Triazacyclononanetricarbonylmolybdenum hydride perchlorate, 3185
∗ 1,4,7-Triazacyclononanetricarbonyltungsten hydride perchlorate, 3186
1,2,4-Triazolo[4,3-*a*]pyridine−silver nitrate, 2270
Trihydrazinealuminium perchlorate, 0064
Trihydrazinecadmium chlorate, 3950
Trihydrazinecobalt(II) nitrate, 4205
Trihydrazinenickel(II) nitrate, 4592
Tris(2,2′-bipyridine)chromium(II) perchlorate, 3874
Tris(2,2′-bipyridine)silver(II) perchlorate, 3873
Tris(2,3-diaminobutane)nickel(II) nitrate, 3589
Tris(1,2-diaminoethane)chromium(III) perchlorate, 2619
Tris(1,2-diaminoethane)cobalt(III) nitrate, 2622
Tris(1,2-diaminoethane)ruthenium(III) perchlorate, 2621
Tris(4-methoxy-2,2′bipyridine)ruthenium(II) perchlorate, 3886
Tris(3-methylpyrazole)zinc sulfate, 3540
Tris(1,10-phenanthroline)cobalt(III) perchlorate, 3890
Tris(1,10-phenanthroline)ruthenium(II) perchlorate, 3889
∗ 1,4,7-Trithia[7]ferrocenophene−acetonitrilecopper(I) perchlorate, 3710

See AMMINECHROMIUM PEROXOCOMPLEXES, [14] DIENE-N_4 COMPLEXES CLATHROCHELATED METAL PERCHLORATES, HYDRAZINEMETAL NITRATES METAL PERCHLORATES: organic ligands, POLYAZACAGED METAL PERCHLORATES SOLVATED OXOSALT INCIDENTS, URANYL MACROCYCLIC PERCHLORATE LIGANDS

DropBooks

ANTHRAQUINONE DYES

Mizgireva, S. B., *Chem. Abs.*, 1987, **106**, 139802

In a DTA study of 14 anthraquinone dyes, most had high flash points (225−335°C) and ignition points (320−375°C). Purpurin dianilide [107528-40-5] was exceptional with the much lower values of 110 and 155°C, respectively.

APROTIC SOLVENTS

1. Buckley, A., *J. Chem. Educ.*, 1965, **42**, 674
2. Banthorpe, D. V., *Nature*, 1967, **215**, 1296

Many aprotic (non-hydroxylic) solvents are not inert towards other reagents and care is necessary when using untried combinations of solvents and reagents for the first time. A further potential hazard which should be considered is that some aprotic solvents, notably dimethyl sulfoxide [1] and dimethylformamide [2], as well as having dramatic effects upon reaction rates, may greatly promote the toxic properties of solutes because of their unique ability to penetrate synthetic rubber protective gloves and the skin. Butyl rubber gloves are reputed to be more satisfactory than other types. The ether and cyclic ether solvents are also subject to peroxidation in storage. Individually indexed compounds are:

N,N-Dimethylacetamide, 1656
Dimethylformamide, 1259
† Dimethyl sulfoxide, 0921
† 1,4-Dioxane, 1617
† Furan, 1439
N-Methylformamide, 0866
† Tetrahydrofuran, 1612
Tetrahydrothiophene-1,1-dioxide, 1622

AQUA REGIA

Fawcett, H. H., *Chem. Eng. News*, 1955, **33**, 897, 1406, 1622, 1844

Aqua regia (nitric and hydrochloric acids, 1:4 by vol., a powerful oxidant), which had been used for cleaning purposes, was stored in screw-capped winchesters. Internal pressure developed overnight, one bottle being shattered. Aqua regia decomposes with evolution of gas and should not be stored in tightly closed bottles (and preferably not at all).

See Nitric acid: Alcohols

Sodium

Chatt, J. *Biographical Memoirs*, Royal Society, 1996, 98.

Addition of a piece of sodium to aqua regia produces spectacular sparks.

ARENECYCLOPENTADIENYLIRON(II) PICRATES **$RC_6H_5Fe^{2+}C_5H_5.2C_6H_2(NO_2)_3O^-$**

Federman Neto, A. *et al., An. Acad. Bras. Cienc.*, 1982, **54**, 331–333

The products of condensing substituted benzenes and ferrocene with $Al/AlCl_3$ were isolated as the picrate salts, which were light-sensitive and explosive.

See other PICRATES

ARENEDIAZO ARYL SULFIDES **ArN=NSAr**

See DIAZONIUM SULFIDES AND DERIVATIVES

ARENEDIAZOATES **ArN=NOR**

Houben-Weyl, 1965, Vol. 10.3, 563–564

Alkyl and aryl arenediazoates ('diazoethers') are generally unstable and even explosive compounds. They are produced by interaction of alcohols with (explosive) bis(arenediazo) oxides, or of *p*-blocked phenols with diazonium salts. The thio analogues are similar. Individually indexed compounds are:

Methyl benzenediazoate, 2799
Methyl 4-bromobenzenediazoate, 2737
Methyl 2-nitrobenzenediazoate, 2782
2-(4-Nitrophenoxyazo)benzoic acid, 3601
∗ Potassium methanediazoate, 0449
∗ Potassium 1-phenylethanediazoate, 2964

See related DIAZONIUM SULFIDES AND DERIVATIVES

ARENEDIAZONIUM OXIDES **$N_2^+ArO^-$**

This group of internal diazonium salts (previously named diazooxides) contains those which are, like many other internal diazonium salts, explosively unstable and shock-sensitive materials.

Other early names of the 1,2-diazonium oxides were based on the benzoxadiazole cyclised structure. For a long time it was doubted that 1,2,3-Benzoxadiazoles had existence, outside the speculative mathematics of theoretical chemists, but more recent researches suggest photochemical equilibrium with the diazonium form and possible predominance in non-polar solvents. Equilibrium implies similar explosive powers though it is possible that sensitivities differ.

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Individually indexed compounds are:
Benzenediazonium-4-oxide, 2189
5-Benzoylbenzenediazonium-2-oxide, 3597
3-Bromo-2,7-dinitrobenzo[*b*]thiophene-5-diazonium-4-oxide, 2883
4-Chloro-2,5-dinitrobenzenediazonium 6-oxide, 2066
3,4-Difluoro-2-nitrobenzenediazonium 6-oxide, 2067
3,6-Difluoro-2-nitrobenzenediazonium 4-oxide, 2068
3,5-Dinitrobenzenediazonium 2-oxide, 2087
4,6-Dinitrobenzenediazonium 2-oxide, 2088
3,5-Dinitro-4-hydroxybenzenediazonium 2-oxide, 2090
3,5-Dinitro-2-methylbenzenediazonium-4-oxide, 2666
3,5-Dinitro-6-methylbenzenediazonium-2-oxide, 2667
2,3,5-Trinitrobenzenediazonium-4-oxide, 2072

See DIAZONIUM CARBOXYLATES

5-Diazoniotetrazolide, *also* Benzenediazonium-4-sulfonate

ARYL CHLOROFORMATES (ARYL CARBONOCHLORIDATES) **ArOCO.Cl**

Water

Muir, G. D., private comm., 1968

During the preparation of aryl chloroformates, it is essential to keep the reaction mixture really cold during water washing to prevent vigorous decomposition. Phenyl and naphthyl chloroformates may be distilled, but benzyl chloroformate is too thermally unstable.

2-ARYLIDENEAMINO-4,6-DINITROPHENOL SALTS $(ArCH{=}NC_6H_2(NO_2)_2O)_2M$

1. Srivastan, R. S. *et al.*, *Def. Sci. J.*, 1979, **29**, 91–96
2. Srivastan, R. S., *Def. Sci. J.*, 1982, **32**, 219–223

The 4′-dimethylaminobenzylidene derivatives form explosive cadmium, mercury and zinc salts [1], and the 4′-nitro analogue forms explosive cadmium, cobalt, copper, iron, mercury, nickel and zinc salts of limited thermal stability [2]. All are constituted with a 1:2 metal:ligand ratio.

See 2-Benzylideneamino-4,6-dinitrophenol

ARYLMETALS ArM

This reactive group includes the individually indexed compounds:

∗ 3-Benzocyclobutenylpotassium, 2904
∗ Bis(η-benzene)chromium(0), 3511
∗ Bis(η-benzene)iron(0), 3512
∗ Bis(η-benzene)molybdenum(0), 3514
∗ Bis(cyclopentadienyl)phenylvanadium, 3705
Dicumenechromium(0), 3767
1,3-Dilithiobenzene, 2178
1,4-Dilithiobenzene, 2179
∗ Diphenyldistibene, 3500
Diphenylmagnesium, 3482
Diphenylmercury, 3480
Diphenyltin, 3502
∗ Lithium diphenylhydridotungstate(2−), 3503
∗ Lithium hexaphenyltungstate(2−), 3892
Naphthylsodium, 3253
Phenylgold, 2221
Phenyllithium, 2259
Phenylsilver, 2217
Phenylsodium, 2287
∗ Phenylvanadium(V) dichloride oxide, 2246
Tetraphenyllead, 3850
2-,3- or 4-Tolylcopper, 2745
Triphenylaluminium, 3749
Triphenylchromium tetrahydrofuranate, 3751
∗ Triphenyllead nitrate, 3753

See also ALKYLMETALS

ARYLTHALLIC ACETATE PERCHLORATES $ArTl(OAc)ClO_4$

See Perchloric acid: Ethylbenzene, etc.

1-ARYL-1-VINYLLITHIUM DERIVATIVES $ArC(Li)=CR_1R_2$

Knorr, R. *et al., Tetrahedron Lett.*, 1977, 3969

In the preparation and use of a series of 5 variously substituted 1-aryl-1-vinyllithium derivatives (*Ar* = phenyl, dimethylphenyl or isopropylphenyl; R_1 = H, Me or 4-tolyl; R_2 = D, Me or 4-tolyl), all operations had to be under purified nitrogen to prevent explosion.

See related ALKYLMETALS

ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

1. Bretherick, L. in *Chemical Process Hazards with Special Reference to Plant Design-V*, 1–15, Kneale, M. (Ed.), Symp. Ser. No. 39a, London, IChE, 1975
2. Grewer, T., *Runaway Reactions*, 1981, Paper 2/E, 1–18
3. Coates, C. F. *et al., Runaway Reactions*, 1981, Paper 4/Y, 1–18; *Chem. & Ind.*, 1981, 84–88
4. Dollimore, D., *Chem. & Ind.*, 1981, 196
5. Kohlbrand, H. T., *Chem. Eng. Progr.*, 1985, **81**(4), 52
6. Gustin, J. L., *J. Loss Prev.*, 1993, **6**(5), 275
7. Fukayama, I. *et al., Bull. Fac. Eng. Yokohama Natl. Univ.*, 1984, **33**, 59–68
8. Yoshida, T. *et al., Kogyo Kayaku*, 1987, **48**(5), 311–316 (*Chem. Abs.*, 1988, **108**, 58900)
9. Cronin, J. L. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 113–132, Oxford, Pergamon, 1987
10. Itoh, M., *Kogyo Kayaku*, 1988, **49**(1), 47–52 (*Chem. Abs.*, 1988, **109**, 8938)
11. Kaneko, Y. *et al., Kogyo Kagaku*, 1988, **49**, 168–175 (*Chem. Abs.*, 1988, **109**, 233687)
12. RSST Brochure, Fauske Associates, 1988, Burr Ridge (IL)

Literature sources of information available to early 1974 and related to assessment of reactive chemical hazards are listed, grouped and discussed in relation to the type of information made available and their application to various situations. Eighty references are given, and those considered suitable for the nucleus of a small safety library are indicated. Toxic hazards are not covered [1]. Relatively simple procedures (oven or Dewar flask tests at normal or elevated pressures) can give a good indication of the potential for exothermic decomposition and runaway reaction hazards, as shown by initial exotherm temperatures, quasi-adiabatic self-heating curves and induction times obtained by these methods [2]. A reliable programme to screen existing, new or modified processes or products for thermal instability has been devised, suitable for a small batch manufacturing installation. This involves a progressive series of tests using simple equipment, for which constructional details are given [3]. Certain practical aspects of the programme were criticised [4]. The Dow reactive chemicals testing programme used to assess

DropBooks

the potential hazards in pilot plant operations is outlined [5]. A Rhone Poulenc procedure based on literature, calculation and calorimetry is described in detail [6].

A simple evaluation method has been developed to assess the hazards of substances, including those regarded as non-explosive, involving thermal sensitivity, mechanical energy sensitivity and detonation sensitivity tests [7]. A method has been developed for predicting the fire and explosion hazards of new chemicals based upon two measurements of thermal properties. These are the heat of decomposition by sealed cell DSC, and the extrapolated decomposition onset temperature by ASTM E-537. These results are used in conjunction with scatter diagrams derived from the results of various standard explosive testing methods and known explosive substances [8]. A simple Insulated Exotherm Test for assessing thermal decomposition hazards, and a Power Compensated Dewar Calorimeter for measuring heat release in liquid systems are key elements in a strategy to assess thermal hazards in batch chemical manufacturing operations [9]. The method in [8] above has been further developed by running comparative tests on different DSC and DTA instruments and analysing the results statistically. Some specific practical problems are identified [10]. A method to determine the detonation/deflagration propagation capabilities of moderately unstable (borderline) chemicals using a propagation tube test has been developed, and the results compared with those from standard explosive tests and DSC methods. Added aluminium oxide was used as inert dephlegmator, and its mixtures with ammonium nitrate (95–100%), 1,3-dinitrobenzene (60–70%), 2,4-dinitrotoluene (70–80%), and dinitrosopentamethylene tetramine (70–80%) would propagate detonation, and dibenzoyl peroxide with 10–15% water content would propagate deflagration [11]. A new and relatively simple test instrument, the Reactive System Screening Tool (RSST) for the rapid assessment of self heating and runaway reaction potential has been described. The sample is contained in an open 10 ml spherical glass cell fitted with internal heater, thermocouple, magnetic stirrer and reagent port. The cell fits into a lagging jacket within a sealable 0.5 l stainless outer pressure vessel of 34 bar working pressure which is fitted with pressure sensor, relief line and reagent syringe. The control unit, which may be interfaced with a personal computer, will set heating rates between 0.1°C/min. and very high rates, to simulate exposure of the sample to fire conditions. For volatile materials, back pressure (e.g. 20 bar) may be applied to suppress evaporation effects. The equipment may be used to acquire data applicable to thermal evaluation or to DIERS vent-sizing purposes, and the test results are comparable with those from other thermal assessment tests. Reults for methanol–acetic anhydride, and for styrene–benzoyl peroxide systems are presented graphically [12].

See PRESSURE RELIEF (reference 6)

The last decade has seen great and rapid advances in many of the specialised areas of this broad topic, and some of these are covered in the topic headings:

∗ACCELERATING RATE CALORIMETRY
CALORIMETRY
CHEMICAL STABILITY/REACTIVITY ASSESSMENT
COMPUTATION OF REACTIVE CHEMICAL HAZARDS
EXOTHERMIC DECOMPOSITION REACTIONS

HEAT FLOW CALORIMETRY
HIGH RATE DECOMPOSITION
MAXIMUM REACTION HEAT
PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION
REACTION SAFETY CALORIMETRY
RUNAWAY REACTIONS
THERMAL EXPLOSIONS
SCALE OF WORK
THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS
THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

ATOMIC ABSORPTION SPECTROSCOPY (AAS)

1. Bretherick, L., *Hazards in the Chemical Laboratory*, 34, London, Royal Society of Chemistry, 3rd edn., 1981
2. Everett, K., *Chem. Brit.*, 1983, **19**, 108
3. Melucci, R. C., *J. Chem. Educ.*, 1983, **60**(3), 238
4. Everson, R. J., *Chem. Eng. News*, 1987, **65**(25), 2
5. Anon., *Fire Prev.*, 1988, (213), 44–45

Care is necessary with acetylene-fed AAS burners to prevent air being drawn up the liquid drainage line, when explosion is likely [1]. While setting up an AAS instrument for use with nitrous oxide–acetylene, an explosion occured shortly after switching from compressed air to the oxide, when the flame became unstable. This was attributed to the outdoor location of the nitrous oxide cylinder (at 5°C) and the expansion cooling (4°C) occurring in the reducing valve, combining to reduce the oxide flow to the point of flame instability and flashback [2]. It was proposed that in student laboratories, air–acetylene flame sources should be replaced by air–natural gas flames to improve safety aspects with very little fall-off in detection limits in instrumental AA metal determinations [3]. Three further incidents involving explosions in AAS installations are reported. One involved accidental contamination of the acetylene inlet line by liquid acetone from an overfilled acetylene cylinder. The other explosions involved leakage of acetylene gas inside the instrument cases and ignition by the electrical controls. Fitting of acetylene sensors inside such instruments to prevent further incidents is suggested [4]. Acetylene gas leaking from a supply tube was ignited by the source flame and a minor explosion occurred, and appears to have damaged both gas supply lines, which led to a second major explosion and fire. This involved some 6 m^3 of acetylene and 18 m^3 of nitrous oxide, and caused severe structural damage [5].

See Perchloric acid: Acetylene, Nitrous oxide
See Silver acetylide (reference 3)

AUTOIGNITION INCIDENTS

Some incidents which have involved autoignition under unexpected circumstances may be found under the entries:
Calcium stearate, 3896
Methaneboronic anhydride–pyridine complex, 0427

Phenylchlorodiazirine, 2673
Thiophosphoryl chloride difluoride, 3980
See MILK POWDER

AUTOIGNITION TEMPERATURE

1. Hilado, C. J. *et al., Chem. Eng.*, 1972, **79**(19), 75–80
2. *Fire Hazard Properties of Flammable Liquids, Gases, Solids*, No. 325M, Boston, NFPA, 1969
3. Shimy, A. A., *Fire Technol.*, 1970, **6**, 135–139
4. Madej, T. *et al., Chem. Abs.*, 1978, **89**, 203300
5. Hilado, C. J. *et al., Fire Technol.*, 1972, **8**, 218–227
6. Bodurtha, 1980, 29
7. Hedden, K. *et al., Chem. Ing. Tech.*, 1979, **51**, 806–809
8. Lewis, D. J., *Proc. 7th Symp. Chem. Process Hazards*, Symp. Ser. No. 58, 257–271, Rugby, IChE, 1980
9. Affens, W. A. *et al., Loss Prev.*, 1980, **13**, 83–88
10. Coffee, R. D., *Loss Prev.*, 1980, **13**, 74–82
11. D'Onofrio, E. J., *Loss Prev.*, 1980, **13**, 84–97
12. Sheldon, M., *Fire Prev.*, 1983, (161), 31–37
13. Suzuki, T., *Fire Mater.* 1994, **18**(2), 81
14. Ashmore, F. S. *et al., Loss Prev. Bull.*, 1987, (075), 1–10
15. Snee, T. J., *Loss Prev. Bull.*, 1988, (091),25–38
16. Bond, 1991, 21

Autoignition temperature (AIT) is the temperature at which a material in contact with air undergoes oxidation at a sufficiently high rate to initiate combustion without an external ignition source. Although only those compounds with unusually low AIT's (225°C or below) have been included in this Handbook, there is a compilation of data for over 300 organic compounds, which also includes the theoretical background and discussion of the effect of variations in test methods upon AIT values obtained [1]. Further AIT data are given in the tabulated publication [2]. Semi-empirical formulae, based only on molecular structure, have been developed which allow AITs to be calculated for hydrocarbons and alcohols, usually with a reasonable degree of accuracy. Flammability limits, flash points, boiling points and flame temperatures may also be calculated for these classes [3]. An equation has been developed which relates the AIT of vapours and gases to the reciprocal of their induction times to self ignition [4]. The effect of iron oxide in lowering the AITs of 21 organic compounds to around 290°C [5] may mean in practical terms that this is the maximum AIT for organic compounds in contact with rusted steel or iron [6].

An improved method for determining the AIT of solids has been described, and the effect of catalytically active inorganics on the reactivity and ignition temperature of solid fuels has been studied. Sodium carbonate markedly lowers the ignition temperatures of coal and coke [7]. The volume of the vessel (traditionally a 200 ml flask) used to determine AIT has a significant effect on the results. For volumes of

$1m^3$ or greater, AIT values are appreciably lower than those measured in the standard equipment, and due allowance should be made for this [8]. The importance of the cool flame in the 2-stage autoignition process has been reviewed [9], and the transition of the cool flame via an intermediate blue flame to the hot ignition stage is discussed in detail [10]. The relationships of the 2 stages were studied for ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol and bis(2-methoxyethyl) phthalate. The latter was observed to give a transition from a cool flame to a hot flame 122°C below its minimum AIT [11]. The topic, including theoretical background, variations in testing methods and application of results, has been surveyed and summarised [12]. A procedure for calculating autoignition temperatures of organics from molecular properties. Good agreement is claimed for most of the 250 compounds examined [13].

In a further survey of AITs and their practical application, the four main factors affecting the AIT are given as: the temperature of surfaces in contact with the mixture; the contact time between these; whether the surface is active or inert; contaminants which enhance or inhibit combustion [14]. AITs are pressure sensitive, generally decreasing with increased air pressure, as also with oxygen enrichment [16]. The values determined for the various fire-related properties of combustibles (flash point, flammability limits, minimum ignition energy, and autoignition temperature) are all dependent on the particular methods used for determination, and this is especially true of the latter values, where the factors affecting the result are not well understood. The relationship between vessel size and the AITs determined therein has been studied experimentally, together with the kinetics of the slow oxidation processes which lead to ignition. Practical methods to reduce the risk of autoignition, specifically in resin manufacture are discussed, but similar considerations are likely to apply to any process involving hot fuel–air mixtures [15].

DropBooks

AUTOXIDATION

1. Davies, 1961, 11
2. Ingold, K. U., *Chem. Rev.*, 1961, **61**, 563
3. Kirk-Othmer, 1978, Vol. 3, 128–133

Autoxidation (interaction of a substance with molecular oxygen at below 120°C without flame [1]) has often been involved in the generation of hazardous materials from reactive compounds exposed to air. Methods of inhibiting autoxidation of organic compounds in the liquid phase has been reviewed [2,3].

See PEROXIDISABLE COMPOUNDS, α-PHENYLAZO HYDROPEROXIDES
α-Phenylazobenzyl hydroperoxide, 3609
Oxygen: Cyclohexane-1,2-dione bis(phenylhydrazone), 4831

AZIDE COMPLEXES OF COBALT(III)

1. Druding, L. F. *et al., J. Coord. Chem.*, 1973, **3**, 105
2. Druding, L. F. *et al., Anal. Chem.*, 1975, **47**(1), 176–177
3. Siebert, H. *et al., Z. Anorg. Chem.*, 1982, **489**, 77–84

A series of 12 complexes of Co(III) with both ionic and covalent azide groups was prepared and most were easily detonable as dry salts, especially at elevated temperatures [1]. Polarography is an accurate and safe method of analysis for azides [2]. Hexaammine-cobalt, -chromium and -rhodium hexaazidocobaltates are explosive, particularly in the dry state [3].

See also AMMINEMETAL AZIDES

See related METAL AZIDES

AZIDES $-N_3$

Many compounds of both organic and inorganic derivation, which contain the azide function, are unstable or explosive under appropriate conditions of initiation, not all have been given entries. The large number of compounds having entries has been subdivided for convenience on the basis of structure.

ACYL AZIDES, AMMINECOBALT(III) AZIDES, AZIDE COMPLEXES OF COBALT(III)

METAL AZIDES, NON-METAL AZIDES

ACYL AZIDES, 2-AZIDOCARBONYL COMPOUNDS, ORGANIC AZIDES

2-AZIDOCARBONYL COMPOUNDS $CO-C-N_3$

1. Boyer, J. H. *et al., Chem. Rev.*, 1954, **54**, 33
2. Weyler, J. *et al., J. Org. Chem.*, 1973, **38**, 3865

Certain 2-azidocarbonyl compounds and congeners have long been known as unstable substances [1]. Some members of a group of 2,5-dialkyl-3,6-diazido-1,4-benzoquinones decompose violently on melting [2]. Individually indexed compounds are:

Azidoacetaldehyde, 0772
Azidoacetic acid, 0774
Azidoacetone, 1190
Azidoacetone oxime, 1215
2,5-Diazido-3,6-dichlorobenzoquinone, 2054
∗ Ethyl α-azido-*N*-cyanophenylacetimidate, 3397
Ethyl 2-azido-2-propenoate, 1890
Ethyl 2,3-diazidopropionate, 1903
Tetraazido-1,4-benzoquinone, 2633

See 2-AZIDO-2-FLUOROCARBOXYLATES

2-AZIDO-2-FLUOROCARBOXYLATES $N_3CFRCOOR'$

Preparative hazard

Takeuchi, Y. *et al., J. Fluorine Chem.*, 1994, **68**(2), 149

The activating effect of the azide makes the fluorine labile, so that there is a risk of excess azide incorporation when attempting preparation by nucleophilic substitution of bromofluorocarboxylates, giving more explosive products than anticipated.

See ORGANIC AZIDES, 2-AZIDOCARBONYL COMPOUNDS

AZIRIDINES

Several derivatives of the highly reactive aziridine (ethylenimine) show explosive instability. Individually indexed compounds are:

† Aziridine, 0863
1,1′-Biaziridinyl, 1593
Bis(*O*-salicylidenaminopropylaziridine)iron(III) perchlorate, 3853
1-Bromoaziridine, 0783
1-Chloroaziridine, 0786

See other STRAINED-RING COMPOUNDS

AZOCARBABORANES

Aono, K. *et al., J. Chem. Soc., Dalton Trans.*, 1981, 1190–1195

In the preparation of 1,1′-azo-2-R-1,2-dicarbadodecaborane(14) by oxidation of the aminocarbaborane anions in liquid ammonia, toluene or other inert solvent must be added before evaporation of ammonia to prevent explosions. Individually indexed compounds are:

1,1′-Azo-1,2-dicarbadecaborane(14), 1796
1,1′Azo-2-phenyl-1,2-dicarbadecaborane(14), 2624

AZO COMPOUNDS C−N=N−C

Vasin, A. Ya. *et al., Chem. Abs.*, 1983, **99**, 39872

The lower concentration limits for ignition of air suspensions of 9 azo dyes have been studied. Individually indexed members of the group of unstable azo compounds are:

4-Aminophenylazobenzene, 3487
Azobenzene (Diphenyldiazene), 3483
2,2′-Azobis(2-amidiniopropane) chloride, 3089
2,2′-Azobis(2-amidiniopropane) peroxodisulfate, 3091
2,2′-Azobis(2,4-dimethylvaleronitrile), 3668
Azo-*N*-chloroformamidine, 0792
2,2′-Azo-3,5-dinitropyridine, 3238
Azoformaldoxime, 0815
Azoformamide, 0816
Azoisobutyronitrile, 3011
2,2′-Azoisovaleronitrile, 3345
Azomethane, 0910
Azo-*N*-methylformamide, 1601
Azo-*N*-nitroformamidine, 0825
3,3′-Azo-(1-nitro-1,2,4-triazole), 1401

∗ 2-Azoxyanisole, 3653
∗ α-(4-Bromophenylazo)benzyl hydroperoxide, 3606
∗ α-(4-Bromophenylazo)phenylethyl α-hydroperoxide, 3648
∗ 2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3156
1-(4-Chloro-2-nitrobenzeneazo)-2-hydroxynaphthalene, 3697

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5-(Diazomethylazo)tetrazole, 0719
Dicyanodiazene, 1005
Diethyl azoformate, 1528
5-(4-Dimethylaminobenzeneazo)tetrazole, 3161
Dimethyl azoformate, 1528
3,4-Dimethyl-4-(3,4-dimethyl-5-isoxazolylazo)isoxazolin-5-one, 3309
1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3702
∗ Diphenyldistibene, 3500
∗ 2,2-Diphenyl-1,3,4-thiadiazoline, 3647
∗ Disodium dicyanodiazenide, 1006
Disodium 5-tetrazolazocarboxylate, 1012
∗ Isopropyldiazene, 1274
∗ Methyldiazene, 0474
Methyl 3-methoxycarbonylazocrotonate, 2830
∗ α-Phenylazobenzyl hydroperoxide, 3609
∗ α-Phenylazo-4-bromobenzyl hydroperoxide, 3607
∗ α-Phenylazo-4-fluorobenzyl hydroperoxide, 3608
∗ Potassium azodisulfonate, 4663
Potassium 4-nitrobenzeneazosulfonate, 2175
Silver 1-benzeneazothiocarbonyl-2-phenylhydrazide, 3605
Sodium 5(5′-hydroxytetrazol-3′-ylazo)tetrazolide, 0682

N-AZOLIUM NITROIMIDATES $N^+-N^--NO_2$

1. Katritzsky, A. R. *et al., J. Chem. Soc., Perkin Trans 1*, 1973, 2624–2626
2. University of Southern California, *Chem. Abs.* 1994, **120**, 80853

Some of the internal salts derived from *N*-heterocycles are dangerously explosive solids, sensitive to modest heating and to impact, also liable to violent spontaneous decomposition, even in solution. A related *N*-nitroimide (hetero-N−NH−NO_2) was also explosive. It is possible the benzotriazolium imidates were also, in fact, the tautomeric nitroaminobenzotriazoles. None of their potassium salts exploded [1]. Related chemistry has been examined with a view to new explosives, in particular 1,4-bis(nitroamino)-1,4-diazabicyclo[2.2.2]octane, said to be surprisingly stable.The individually indexed unstable compounds are:

Benzimidazolium 1-nitroimidate, 2704
Benzotriazolium 1-nitroimidate, 2281
Benzotriazolium 2-nitroimidate, 2282
4-Nitroamino-1,2,4-triazole, 0777

See other HIGH-NITROGEN COMPOUNDS, *N*-NITRO COMPOUNDS

BENZENE ISOMERS C_6H_6

Editor's comments.

There are some 40 structural isomers which seem stable enough to be isolated. Six enjoy individual entries in Part I, others are less well described. All will be of higher energy than benzene, itself endothermic, all should be suspected

capable of causing explosion. To a lesser degree, non-aromatic isomers of substituted benzenes will also be suspect.

See ENDOTHERMIC COMPOUNDS

BATS

1. Anon., *Chemical Engineer*, 1993, 546/7, 33
2. Various, *Chem. Eng. News*, 1993, **71**(38), 64; **71**(41), 60

An explosion demolishing an empty building was dubiously attributed to ignition of methane evolved from bat droppings [1]. There was much argument as to the probability of this [2], the eventual conclusion being that sewer gas from a septic tank was responsible.

See also INDIGESTION

BATTERIES

1. Anon., *Loss Prev. Bull.*, 1992, (108), 28
2. Anon., *Universities' Safety Assoc. Safety News*, 1979, (12), 20–21
3. *See entries under* Lithium
4. *Battery Hazards and Accident Prevention*, Levy, S. C. & Bro, P., New York, Plenum Press, 1994

Electrical batteries have associated explosion dangers. These are best known as gas evolution and explosion consequent upon over charging during recharge [1] or connection with reversed polarity: Of 3 HP7 zinc-carbon batteries inserted into a calculator, one was inserted wrongly with reversed polarity. After 2 days, when it was taken out to rectify the error, the battery 'exploded', the carbon rod being ejected with considerable force [2]. With more powerful cells, the risk is increasingly the chemical energy contained in the cell [3]. Short circuits can also serve as ignition sources in flammable surroundings. A book covering all aspects of safety with many types of cell has been published. It gives accounts of many incidents [3].

Silver: Electrolytes, Zinc; STEEL

BENZYL COMPOUNDS **$PhCH_2-$**

Several benzyl derivatives exhibit potentially hazardous properties arising from the activation by the adjacent phenyl group, either of the substituent or of a hydrogen atom. Halides, in particular, are prone to autocatalytic Friedel Crafts polymerisation if the aromatic nucleus is not deactivated by electron withdrawing substituents.

Individually indexed compounds are:

Barium *N*-perchlorylbenzylamide, 3649
Benzyl alcohol, 2806
Benzylamine, 2812
Benzyl azide, 2779
Benzyl bromide, 2735
Benzyl chloride, 2738
Benzyldimethylamine, 3168

Benzyl fluoride, 2746
Benzyl nitrate, 2765
Benzyloxyacetylene, 3133
∗ Benzylsilane, 2832
∗ Benzylsodium, 2787
1-Benzyl-3-(4-tolyl)triazene, 3657
1,2-Bis(chloromethyl)benzene, 2946
4-Bromomethylbenzoic acid, 2926
2-Chloro-5-nitrobenzyl alcohol, 2715
4-Chloro-2-nitrobenzyl alcohol, 2716
4-Chloro-3-nitrobenzyl alcohol, 2717
5-Chloro-2-nitrobenzyl alcohol, 2718
6-Chloro-2-nitrobenzyl bromide, 2671
2-Chloro-4-nitrobenzyl chloride, 2678
4-Chloro-2-nitrobenzyl chloride, 2679
Dibenzyl ether, 3655
Dibenzyl phosphite, 3658
Dibenzyl phosphorochloridate, 3650
Mercury(II) *N*-perchlorylbenzylamide, 3651
3-Methoxybenzylamine, 2997
4-Methoxybenzyl chloride, 2962
4-Methylbenzyl chloride, 2959
2-Nitrobenzyl alcohol, 2769
3-Nitrobenzyl alcohol, 2770
4-Nitrobenzyl alcohol, 2771
2-Nitrobenzyl chloride, 2713
Phenylacetonitrile, 2935
2,2′-[1,4-Phenylenebis(azidomethylidyne)]bis(propanedinitrile), 3622
Tribenzylarsine, 3822

See also 2-HALOMETHYL-FURANS OR THIOPHENES, NITROBENZYL COMPOUNDS, α-PHENYLAZO HYDROPEROXIDES

BIS(ARENEDIAZO) OXIDES **$(ArN{=}N)_2O$**

1. Bamberger, E., *Ber.*, 1896, **29**, 451
2. Kaufmann, T. *et al.*, *Ann.*, 1960, **634**, 77

Action of alkalies on diazonium solutions, or of acids on alkali diazoates to give a final pH of 5–6, causes these compounds (‘diazoanhydrides’) to separate as oils or solids. Many of these are violently explosive (some exceeding nitrogen trichloride in effect), sensitive to friction and heat or contact with aromatic hydrocarbons [1,2]. Individually indexed compounds are:

Bis(benzeneazo) oxide, 3490
Bis(4-chlorobenzenediazo) oxide, 3456
Bis(toluenediazo) oxide, 3654
Bis(2,4,5-trichlorobenzenediazo) oxide, 3431

See related BIS(ARENEDIAZO) SULFIDES, BELOW

BIS(ARENEDIAZO) SULFIDES **$(ArN{=}N)_2S$**

Some of the products of interaction of diazonium salts with sulfides may have this structure. Relevant entries are:
Bis(benzenediazo) sulfide, 3491
Bis(4-nitrobenzenediazo) sulfide, 3467
See DIAZONIUM SULFIDES AND DERIVATIVES

BIS(DIFLUOROAMINO)ALKYL NITRATES **$F_2NCRCH(NF_2)ONO_2$**

Reed, S. F., *J. Org. Chem.*, 1972, **37**, 3329–3330
Prepared from tetrafluorohydrazine and alkenyl nitrates, these compounds are dangerously explosive. Purification is difficult, as they are sensitive to heat and shock. Preparation by nitration of the alcohol is a more practical route.
See other DIFLUOROAMINO COMPOUNDS

BIS(FLUOROOXY)PERHALOALKANES **$F_3CCCl(OF)_2$ etc.**

Hazardous preparation and products
Sekiya, A. *et al.*, *Inorg. Chem.*, 1980, **19**, 1328–1330
The compounds are all strong oxidants and explosive, requiring very careful handling. Individually indexed compounds are:
1,1-Bis(fluorooxy)hexafluoropropane, 1061
2,2-Bis(fluorooxy)hexafluoropropane, 1062
1,1-Bis(fluorooxy)tetrafluoroethane, 0641
2-Chloro-1,1-bis(fluorooxy)trifluoroethane, 0595
1,1,4,4-Tetrakis(fluoroxy)hexafluorobutane, 1374
See Fluorine: Fluorocarboxylic acids, etc., 4310
See related HYPOHALITES

PrepBooks

BIS(SULFUR)DIIMIDES **$Z(N{=}S{=}NR)_2$**

Appel, R. *et al.*, *Chem. Ber.*, 1976, **109**, 2444
During the preparation of a series of the bis(diimides), ($Z = (CH_2)_{2\text{ or }3}$; R = Me, Et), work-up operations must be at below 100°C to avoid violent decomposition.
See other N–S COMPOUNDS

BITUMEN

1. Agaev, A. S. *et al.*, *Chem. Abs.*, 1975, **82**, 88310
2. Hoban, T. W. S. *et al.*, *J. Loss Prevention*, 1994, **7**(3), 217

Factors leading to ignition or explosion during preparation of high-melting bitumens by air-blowing petroleum residues were identified as control of vapour temperature (often above AIT), presence of lower hydrocarbon vapours, and lack of control of free oxygen content. Measures for controlling these are discussed [1]. Bitumen storage tank fires are instanced, and the causes discussed [2]
See Oxygen: Hydrocarbons

BLEACHING POWDER **$Ca(OCl)_2,4H_2O.CaCl_2,Ca(OH)_2,H_2O$**

1. Mellor, 1956, Vol. 2, Suppl. 1, 564–567
2. *Accid. Bull. No. 30*, Washington, Amer. Railroad Assoc. Bur. Explos., 1921
3. Gill, A. H., *Ind. Eng. Chem.*, 1924, **16**, 577
4. 'Leaflet No. 6', London, Inst. Chem., 1941

Bleaching powder is effectively a mixture of calcium hypochlorite, calcium hydroxide and a non-hygroscopic form of calcium chloride [1] and may therefore be regarded as a less active form (39% available chlorine) of oxidant than undiluted calcium hypochlorite (49% chlorine). There is a long history of explosions, many apparently spontaneous, involving bleaching powder. On storage or heating, several modes of decomposition are possible, one involving formation of chlorate which may increase the hazard potential. Of the 3 possible routes for thermal decomposition, that involving liberation of oxygen predominates as the water content decreases, and at 150°C the decomposition becomes explosive [1]. Material which has been stored for a long time is liable to explode on exposure to sunlight, or on overheating of tightly packed material in closed containers [2]. The spontaneous explosion of material packed in drums was attributed to catalytic liberation of oxygen by iron and manganese oxides present in the lime used for manufacture [3]. Traces of metallic cobalt, iron, magnesium or nickel may also catalyse explosive decomposition [1]. When the lever-lid of a 6-month-old tin of bleaching powder was being removed, it flew off with explosive violence, possibly owing to rust-catalysed slow liberation of oxygen [4].

Bis(2-chloroethyl) sulfide

Mellor, 1956, Vol. 2, Suppl. 1, 567

Interaction is very exothermic and ignition may occur, particularly in presence of water.

Wood

Anon., *ABCM Quart. Safety Summ.*, 1933, **4**, 15

A mixture of sawdust and bleaching powder ignites when moistened.

See other METAL HYPOCHLORITES, OXIDANTS

BLEVE

1. Prugh, R. W., *Chem. Eng. Progress*, 1991 (Feb.), 66
2. Venart, J. E. S. *et al., Process Safety Progr.*, 1993, **12**(2), 67
3. Birk, A. M. *et al., J. Loss Prev.*, 1994, **7**(6), 474
4. Birk, A. M. *et al., Chem. Abs.*, 1998, **129**, 323897d

A Boiling Liquid Expanding Vapour Explosion, or BLEVE, is an industrial event related to the laboratory 'bump' occasioned when the inadequately mixed bottom of a vessel of liquid becomes superheated, then explosively boils. In the industrial version, rupture of a pressurised container is usually involved. Although strictly speaking a non-reactive physical hazard, chemical fires and explosions, with fatalities, often follow. Means of estimating risk and prevention, with a list of incidents are given[1]. A more ferocious version, the Boiling Liquid Compressed Bubble

Explosion, or BLCBE, involving multiple site initiation during the explosive stage, is described [2]. A study of Bleves in propane tanks is combined with a procedure for predicting whether a tank will BLEVE or merely produce a jet leak on overheating [3]. The relationship between BLEVE conditions and subsequent fireballs has been studied [4]

See also VAPOUR CLOUD EXPLOSIONS

BLOWING AGENTS

1. Morisaki, S. *et al., J. Haz. Mat.*, 1981, **5**, 49–63
2. Bond, J., *Hazards from Pressure*, IChE Symp. Ser. No. 102, 37–44, Oxford, Pergamon, 1987

Six blowing agents (* in the list below), which generate gas (mainly N_2) by thermal decomposition and are used to create plastic foams, were examined by DSC at up to 50 bar pressure. The very significant increase in heat release under pressure (especially air pressure) suggests that sealed containers of the materials may explode violently if subjected to heating [1]. Decomposition of a hydrazide blowing agent in a large feed hopper was probably initiated by friction from the mechanical feed-screw in the base. The exothermic decomposition activated the explosion suppression system which added to the volume of gas produced and caused rupture of the hopper [2].

Individually indexed compounds are:
2,2′-Azobis(2,4-dimethylvaleronitrile), 3668
Azoformamide*, 0816
Azoisobutyronitrile*, 3011
2,2′-Azoisovaleronitrile*, 3345
Azo-*N*-methylformamide, 1601
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane*, 1954
4,4′-Oxybis(benzenesulfonylhydrazide)*, 3525
4-Toluenesulfonylhydrazide*, 2827

See also RADICAL INITIATORS

DropBooks

BORANES (BORON HYDRIDES)

Wright, S. W. *et al., Chem. Eng. News*, 1992, **70**(35), 4

Many boranes and their complexes are air sensitive and pyrophoric. Boranes and their complexes apparently disproportionate to higher boranes and hydrogen on storage, pressurising their containers.

Aluminium chloride, Sulfur dioxide

Bonnetot, B. *et al., Inorg. Chim. Acta*, 1989, **156**(2), 183

Intimate mixtures or complexes of the above and salts of decahydrodecaborate(2–) left after evaporation of excess liquid sulfur dioxide exploded on grinding. The same could presumably happen with derivatives of other boranes.

Carbon tetrachloride

1. Hermanek, S., *Chem. Abs.*, 1976, **84**, 38384
2. *491M*, 1975, 92

Carbon tetrachloride is not recommended as an eluting solvent in the chromatographic separation of boranes, carbaboranes or their derivatives because of the danger of explosion [1]. Use of a carbon tetrachloride extinguisher on a diborane fire caused a violent explosion [2].

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See also ALKYLBORANES, ALKYLHALOBORANES, HALOBORANES

Individually indexed compounds are:

∗ Ammonium decahydrodecaborate(2−), 0199
∗ 1,1′-Azo-[2-methyl-1,2-dicarbadecaborane(14)], 2624
∗ Bis(borane)−hydrazine, 0143
∗ Bis(dimethylaminoborane)aluminium tetrahydroborate, 1795
∗ *N,N′*-Bis(trimethylsilyl)aminoborane, 2612
Borane, 0135
∗ Borane−ammonia, 0141
∗ Borane−bis(2,2-dinitropropylhydrazine), 0137
Borane−dimethylsulfide, 0136
∗ Borane−hydrazine, 0142
∗ Borane−phosphorus trifluoride, 0140
∗ Borane−pyridine, 0139
∗ Borane−tetrahydrofuran, 0138
∗ *N*-*tert*-Butyl-*N*-trimethylsilylaminoborane, 2878
∗ *B*-Chlorodimethylaminodiborane, 0962
∗ Cyanoborane oligomer, 0393
Decaborane(14), 0198
∗ Diammineboronium heptahydrotetraborate, 0190
∗ Diammineboronium tetrahydroborate, 0167
† Diborane(6), 0166
∗ Dimethylaminodiborane, 0967
∗ Disodium tridecahydrononaborate(2−), 0195
∗ Heptakis(dimethylamino)trialuminium triboron pentahydride, 3676
Hexaborane(10), 0191
Hexaborane(12), 0192
Pentaborane(11), 0189
† Pentaborane(9), 0188
∗ Phosphorus azide difluoride−borane, 4316
Poly[borane(1)], 0134
Tetraborane(10), 0181
∗ Tetraphosphorus hexaoxide−bis(borane), 4868

See 1,3-DIAZA-2-BORACYCLOALKANES *See other* NON-METAL HYDRIDES

BORON COMPOUNDS

This class contains the groups:

ALKYLBORANES, ALKYLHALOBORANES
AZOCARBABORANES, BORANES, CARBABORANES
DIAZONIUM TETRAHALOBORATES, HALOBORANES

tert-BUTYL ESTERS $Me_3COCO.R$

Hodgson, P. K. G. *et al., J. Chem. Soc., Perkin Trans. 2*, 1978, 854
Preparation of *tert*-butyl esters from the acid and 2-methylpropene under pressure in glass vessels led to explosions. A safe procedure in a steel cylinder is described.

tert-BUTYL PEROXOPHOSPHATE DERIVATIVES $Me_3COOP(O)(OR)_2$

Rieche, A. *et al., Chem. Ber.*, 1962, **95**, 381–388
Although dialkyl *tert*-butylperoxophosphate derivatives are relatively stable, the diaryl esters and bis(*tert*-butylperoxo) esters decompose violently on attempted isolation. Individually indexed compounds are:
O–*O*-*tert*-Butyl diphenyl monoperoxophosphate, 3712
O–*O*-*tert*-Butyl di(4-tolyl) monoperoxophosphate, 3763
tert-Butyl peroxophosphoryl dichloride, 1644
Di(*O*–*O*-*tert*-butyl) ethyl diperoxophosphate, 3374
See related PEROXYESTERS, PHOSPHORUS ESTERS

DropBooks

CALORIMETRY

Individual entries:

ACCELERATING RATE CALORIMETRY (ARC)
ADIABATIC CALORIMETRY
ASSESSMENT OF REACTIVE CHEMICAL HAZARDS
CHEMICAL STABILITY/REACTIVITY ASSESSMENT
DIFFERENTIAL SCANNING CALORIMETRY (DSC)
DIFFERENTIAL THERMAL ANALYSIS (DTA)
HEAT FLOW CALORIMETRY
OXYGEN BOMB CALORIMETRY
REACTION SAFETY CALORIMETRY
THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

CAN OF BEANS

Foote, C. S., private comm., 1965
An unopened can of beans, placed in a laboratory oven originally at 110°C but later reset to 150°C, exploded causing extensive damage. Comments were judged to be superfluous.
See Diprotium monoxide, 4475

CARBABORANES **(Cyclic boranes with hetero C atoms)**

Carbon tetrachloride
See BORANES: carbon tetrachloride

CARBONACEOUS DUSTS

Explosion and Ignition Hazards, Rept. 6597, Washington, US Bur. Mines, 1965
Hazards of 241 industrial dusts which may explode or burn because of their carbon content are defined, covering particle size and chemical composition in 10 categories.
See also DUST EXPLOSION INCIDENTS, PETROLEUM COKE
Carbon, (reference 6), 0298

CARBONYLMETALS **$M(CO)_n$**

Bailar, 1973, Vol. 1, 1227
The explosive 'carbonylalkali-metals', previously formulated as monomeric compounds, are either dimeric acetylene derivatives of the general formula MOC≡COM, or are trimers of the latter and formulated as salts of hexahydroxybenzene. Many true carbonylmetal complexes are air-sensitive and pyrophoric, not always immediately. Individually indexed compounds are:

Bis(dicarbonylcyclopentadienyliron)−bis(tetrahydrofuran)magnesium, 3835
∗ Bis[dicarbonyl(cyclopentadienyl)tributylphosphinemolybdenum]−tetrakis (tetrahydrofuran)magnesium, 3913
∗ Bis(2-methyl-1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3833
∗ Bis(1,8-naphthyridine)tetracarbonyldirhodium(I) perchlorate, 3791
∗ Caesium pentacarbonylvanadate(3−), 1811
∗ Carbonyl(pentasulfur pentanitrido)molybdenum, 0535
Decacarbonyldirhenium, 3386
∗ Dicarbonyl-π-cycloheptatrienyltungsten azide, 3123
∗ Dicarbonylmolybdenum diazide, 0995
∗ Dicarbonyl-η-trichloropropenyldinickel chloride dimer, 3233
∗ Dicarbonyltungsten diazide, 1013
Dodecacarbonyltetracobalt, 3420
Dodecacarbonyltriiron, 3428
Hexacarbonylchromium, 2056
Hexacarbonylmolybdenum, 2628
Hexacarbonyltungsten, 2636
Hexacarbonylvanadium, 2635
∗ Hexakis(pyridine)iron(II) tridecacarbonyltetraferrate(2−), 3906
∗ Lithium octacarbonyltrinickelate, 3109
Nonacarbonyldiiron, 3111
Octacarbonyldicobalt, 2881
† Pentacarbonyliron, 1814
∗ Potassium pentacarbonylvanadate(3−), 2049

∗ Potassium tricarbonyltris(propynyl)molybdate(3−), 3471
∗ Sodium pentacarbonylrhenate, 2051
∗ Sodium tetracarbonylferrate(2−), 1376
∗ Tetracarbonylmolybdenum dichloride, 1358
† Tetracarbonylnickel, 1805
∗ Tetrakis(pyridine)bis(tetracarbonylcobalt)magnesium, 3867
∗ 1,4,7-Triazacyclononanetricarbonylmolybdenum hydride perchlorate, 3185
∗ 1,4,7-Triazacyclononanetricarbonyltungsten hydride perchlorate, 3186
∗ Tris(bis-2-methoxyethyl ether)potassium hexacarbonylniobate(1−), 3856

CATALYST HANDLING SAFETY

1. Fulton, J. W., *Chem. Eng* . (NY), 1987, **94**(12), 99−101
2. Habermehl, R., *Chem. Eng. Progr*., 1988, **84**, 16−19
3. Reynolds, M. P. *et al.*, *Chem. Ind* . (Dekker), 1996, **68**, 371

Safety aspects of drum storage, pellet screening, dust removal, reactor loading and unloading, and activation of process catalysts are discussed [1], and reprocessing aspects are considered, with disposal as a last resort [2]. Hydrogenation catalysts introduce their own problems [3].

See also HYDROGENATION CATALYSTS

CATALYTIC HYDROGENATION AUTOCLAVES

Harak, J., *Stud. Surf. Sci. Catal.*, 1986 (27, Catal. Hydrog.), 578−611

Measures and equipment needed for safe control of autoclaves used for laboratory, pilot plant, or industrial scale catalytic hydrogenation are discussed, including the need for early recognition of onset of hazardous conditions.

DropBooks

CATALYTIC NITRO REDUCTION PROCESSES
HYDROGENATION CATALYSTS
HYDROGENATION INCIDENTS

CATALYTIC IMPURITY INCIDENTS

Incidents where presence of impurities, often in trace (catalytic) amounts, has significantly reduced stability or enhanced reactivity are under the entries:

Acetic anhydride, : Ethanol, Sodium hydrogen sulfate, 1534
† Acrylaldehyde, 1145
Adipic acid, 2441
Ammonium perchlorate, : Impurities, 4004
Azidoacetic acid, 0774
† Aziridine, : Acids, 0863
Benzoyl azide, 2698
Benzyl chloroformate, 2931
1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0803
Bromine trioxide, 0259
2-Butanone oxime, 1654
2-Butyne-1,4-diol, 1526

Butyraldehyde oxime, 1655
Carbon, : Unsaturated oils, 0298
Chlorine, : Carbon disulfide, 4047
† 1-Chloro-2,3-epoxypropane, : Contaminants, 1162
Cyanogen chloride, 0323
∗ Diethyl phosphorochloridate, 1681
† 1,1-Difluoroethylene, 0700
† Diketene, : Acids, or Bases, or Sodium acetate, 1441
N,N-Dimethylacetamide, 1656
2,4-Dinitrotoluene, 2726
4-Ethoxy-2-methyl-3-butyn-2-ol, 2844
Ethylene oxide, : Contaminants, 0829
Ethyl oxalyl chloride, 1456
Hydrogen peroxide, : Coal, 4477
Hydrogen peroxide, : Copper(II) chloride, 4477
† Isopropyl chloroformate, 1560
Maleic anhydride, : Bases, or Cations, 1404
Mercury(II) oxalate, 0982
Methylammonium nitrate, 0506
4-Methylbenzyl chloride, 2959
∗ Methyl isocyanoacetate, 1470
N-Methylmorpholine oxide, 1997
Nickel, : Hydrogen, Oxygen, 4820
Nitric acid, : Sulfur dioxide, 4436
Oxygen (Gas), : Carbon disulfide, Mercury, Anthracene, 4831
Oxygen (Liquid), : Carbon, Iron(II) oxide, 4832
Oxygen difluoride, : Hexafluoropropene, Oxygen, 4317
Potassium chlorate, : Manganese dioxide, 4017
† Propionyl chloride, : Diisopropyl ether, 1163
† Propylene oxide, : Sodium hydroxide, 1225
Silver azide, 0023
Silver nitride, 0038
Sodium carbonate, 0552
Sodium peroxoborate, 0155
Tetrafluoroammonium tetrafluoroborate, 0133
Triallyl phosphate, 3184
Trifluoromethanesulfonic acid, : Acyl chlorides, Aromatic hydrocarbons, 0375
Trimethyl phosphate, 1318

See DIAZONIUM TETRAHALOBORATES (reference 5)
See INDUCTION PERIOD INCIDENTS

CATALYTIC NITRO REDUCTION PROCESSES $RNO_2 \rightarrow RNH_2$

1. MacNab, J. I., *Runaway Reactions*, 1981, Paper 3/S, 1–15
2. Stoessel, F., *J. Loss Prev.*, 1993, **6**(2), 79

Catalytic reduction of aromatic nitro compounds to the amines is highly exothermic ($\Delta H = -548 \pm 12$ kJ/mol) and has high potential for hazard in the event of cooling- or other process-failure. The total reaction proceeds *via* nitroso and hydroxylamino intermediates, both of which are reactive and may undergo undesired condensation or disproportionation reactions, and the thermochemistry of all these possibilities was investigated. The reduction or disproportionation of the hydroxylamino intermediate (which is of low thermal stability) is identified as the fastest and most exothermic step (despite which it can frequently be concentrated or trapped); implications for process safety are considered in detail and verified by experiment with typical compounds and intermediates [1]. A calorimetric study of the hazards inherent in hydrogenation of nitroaromatics was made, using nitrobenzene as model compound [2]. Individual incidents of this type are:
2-Chloro-5-methylphenylhydroxylamine, 2796
3,4-Dichlorophenylhydroxylamine, 2243
2-Nitroanisole, : Hydrogen
1,1,1-Tris(azidomethyl)ethane, 1937
Tris(hydroxymethyl)nitromethane, 1664
See also CATALYTIC HYDROGENATION AUTOCLAVES, CALORIMETRY

CATHODIC CORROSION PROTECTION

Bond, 1991, 43; *ibid.*, 63
Cathodic protection systems have started a number of hydrocarbon fires, either by direct current sparking to earth, or from thermite reactions causing sparks when rusty lumps of iron fall on magnesium electrodes.
See THERMITE REACTIONS

DropBooks

CELLULOSE $(C_6H_{10}O_5)_n$

Gray, B. F. *et al., J. Chem. Technol., Biotechnol.*, 1984, **34A**(8), 453–463
Spontaneous ignition hazards and criteria for safe storage of stockpiles of cellulosic materials were investigated on the laboratory scale, using piles of sieved bagasse pith of various sizes and shapes. Temperature profiles were measured and critical temperatures for ignition determined with high accuracy. The important part played by moisture was investigated, and the need for improvement in scaling extrapolation procedures is stressed. The results are consistent with those for wood flour, and conclusions are applicable to all cellulosic materials at high temperatures.
Energy of exothermic decomposition of finely fibrous cellulose in range 275–335°C was measured as 0.32 kJ/g.
See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

Calcium oxide
See Calcium oxide: Water (reference 2)

Oxidants
See Calcium permanganate: Cellulose

Fluorine: Miscellaneous materials, 4310
Magnesium perchlorate: Cellulose, etc., 4084
N-Methylmorpholine oxide, 1997
Nitric acid: Cellulose, 4436
Perchloric acid: Cellulose and derivatives, 3998
Perchloric acid: Hydrofluoric acid, Structural materials, 3998
Potassium chlorate: Cellulose, 4017
Potassium nitrate: Cellulose, 4650
Sodium chlorate: Paper, etc., or: Wood, 4039
Sodium nitrite: Wood, 4720
Sodium nitrate: Fibrous material, 4721
Sodium peroxide: Fibrous materials, 4803
Zinc permanganate: Cellulose, 4710
BLEACHING POWDER: Wood
PERCHLORATES: Organic matter

Water

1. Longauerova, D. *et al., Chem. Abs* . 1993, **118**, 26762
2. Kletz, T. A., *Process Safety Progress*, 1995, **14**(4), 274

A storage tank for neutral sulphite woodpulp exploded. Investigation showed bacterial contamination, producing hydrogen and hydrogen sulphide in the headspace, which subsequently suffered electrostatic ignition [1]. A similar incident with ignition from welding operations is reported; in this case not bulk wet woodpulp, but recycled water from pulping operations was the source of the hydrogen [2]. [NB, most shirts and all kitchen paper are made of cellulose, neither the above phenomena, nor a very mild exotherm on hydration, justify the statement in another recent work on reactive chemicals that cellulose and water are an unsafe combination — Editor]

See COTTON, WOOD PULP

CELLULOSE NITRATE

(*MCA SD-96*, 1970); *FPA H118*, 1982

1. Kirk-Othmer, 1979, Vol. 5, 129–137
2. Anon., *Accidents*, 1961, **46**, 12
3. Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 13
4. *MCA Case History No. 1614*
5. Fifen, R. A., *Progr. Astronaut. Aeronaut.*, 1984, **90**, 177–237
6. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62–74
7. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
8. Roberts, T. A. *et al., J. Loss Prev.*, 1992, **5**(5), 311
9. Dosoudel, T. *et al., Chem. Abs.*, 1994, **121**, 13250

Cellulose nitrate is very easily ignited and burns very rapidly or explosively, depending on the degree of confinement, degree of nitration and state of subdivision. Unless very pure and stabilised, it deteriorates in storage and may ignite

spontaneously [1]. Removal of the emulsion coating from celluloid film base gives unstable material which may ignite on prolonged storage in an enclosed space [2]. Unused but aged centrifuge tubes made of 'nitrocellulose' plasticised with dibutyl phthalate, ignited and exploded while being steam-sterilised in an autoclave at 125°C. The violent decomposition was attributed to the age of the tubes, the high temperature and the presence of the steam, (leading to hydrolysis and formation of free nitric acid) [3]. During hacksaw cutting of a pipe containing cellulose nitrate residues, a violent explosion occurred [4]. The ignition and combustion chemistry of cellulose nitrate has been reviewed, including the decomposition and catalysis mechanisms [5]. The finely divided nitrate is also a very significant dust explosion hazard, maximum explosion pressures above 17.4 bar, with maximum rate of rise above 1.42 kbar/s have been recorded [6]. Values for the critical ignition temperature of 60 and 41°C for induction periods of 7 and 60 days, respectively, have been recorded. Autocatalytic combustion is exhibited [7]. Details of storage separation distances for cellulose nitrate sufficient to prevent thermal radiation propagating deflagration from one container to the next are given [8]. Water in nitrocellulose powders does not always have the expected stabilising effects. Detonation velocities can increase and 25% water was shown to facilitate the deflagration to detonation transition [8].

Amines MRH 4.81/tr. (for all 8 amines)

1. Anon., *ABCM Quart. Safety Summ.*, 1956, **27**, 2
2. Thurlow, G. K. *et al.*, private comm., 1973
3. Kaila, E., *Chem. Abs.*, 1958, **52**, 19121$_f$

DropBooks

Cellulose nitrate of high surface area (dry or alcohol-wet guncotton or scrap) spontaneously ignited in contact with various amines used as curing agents for epoxy resins. These included 1,2-diaminoethane, *N*-2-hydroxyethyl-1,2-diaminoethane, diethylenetriamine, triethylenetetramine, *N*-2-hydroxyethyltriethylenetetramine, tetraethylenepentamine, 2-hydroxyethylamine, 2-hydroxyethyldimethylamine, 2-hydroxypropylamine, 3-dimethylaminopropylamine, morpholine, and diethylamine. Ethylamine and dibutylamine caused charring but not ignition [1]. Similar results were found during an investigation of the compatibility of cellulose nitrate with a range of amine and amide components used in paint manufacture. Preliminary small-scale (12 g) tests in which ethyl acetate solutions of cellulose nitrate and the other components were mixed in a lagged boiling tube showed large exotherms (which boiled the solvent off) with 1,4-diazabicyclo[2.2.2]octane, 2,4,6-tris(dimethylamino)phenol, morpholine and benzyldimethylamine. Smaller exotherms were shown by dodecylamine, dodecyldimethylamine (both fat-derived, containing homologues) and a polyamide resin, Versamid 140.

Subsequent tests in which small portions of these undiluted liquid amines and dried cellulose nitrate linters were contacted (with a little added butyl acetate for the solid phenol) under various conditions, gave ignition with the first 3 amines, and exotherms to 110°C with foaming decomposition for the remaining 4. Other amine resin components showed slight or no exotherms in either test [2]. Contact of cellulose nitrate with a little butylamine caused explosive reaction [3].

Iron red pigment, Plasticiser

Penczek, P. *et al.*, *Chem. Abs.*, 1976, **85**, 63924

During roller-blending to disperse iron red pigment (iron(III) oxide) into plasticised cellulose nitrate, the mixture became a gel after 15 passes and tended to self-ignite.

Iron(II) sulfate

Yan, Z., *Chem. Abs.*, 1983, **99**, 106948

Presence of iron(II) sulfate reduces the stability of the nitrate by a factor of 2.5.

Other reactants

Yoshida, 1980, 274

MRH values calculated for 13 materials all indicate likely catalytic decomposition effects with traces of them.

Potassium iodide

Morrow, S. I., *Anal. Calorim.*, 1977, **4**, 185–191

Low levels of potassium iodide strongly retard the thermal decomposition of thin films of cellulose nitrate.

See related ALKYL NITRATES *See other* PYROPHORIC MATERIALS

CHARCOAL

Pfeil, N., *Loss Prevention and Safety Promotion in the Process Industries* , Vol II, (Mewis, J. J., Pasman, H. J. and De Rademaker, E. E. Eds.), 161, Amsterdam, Elsevier, 1995

Autoignition of fresh charcoal, but not gunpowder prepared from it, is known to have happened in the black powder industry. (Optimum charcoal for gunpowder production is well short of being fully carbonised).

See Carbon

CHEMICAL PLANT SAFETY

1. Kirk Othmer, 1996, Vol. 19, 190
2. Ullmann, 1995, B7, B8, especially B8, 311
3. *Loss Prevention in the Process Industries*, Lees, F. P., Oxford, Butterworth-Heinemann, 2nd Edn. (3 Volumes), 1996
4. *The Safe Handling of Chemicals in Industry*, Carson P. A., Mumford, C. J., Harlow (Essex), Longmans 1989: (originally two volumes, later extended to four)

Much writing on this subject, from introductory essays to multivolume books covering all aspects, including the legislatory and bureaucratic, has latterly appeared. Remarkably little of it is directly relevant to the purposes of this book, which is not surprising since it is slips, trips, falls and moving transport accidents which injure and kill chemical workers, far more than do fire and explosion, though these are themselves well ahead of poisoning in the accident statistics. Public concern is otherwise focussed. Some English-language examples are given above.

CHEMICAL STABILITY/REACTIVITY ASSESSMENT

Fenlon, W. J., *Proc. Intern. Sympos. Prev. Major Chem. Accid.*, Washington, 1987, A.27–A.41, New York, AIChE, 1987

In the Technical Safety Laboratory of Eastman Kodak, the role played by calorimetric methods (such as High Pressue DSC and ARC techniques) in assessing the stability of chemicals and processes, though a central one, is but part of a range of techniques used for this overall purpose. The relations between these methods is discussed and presented in the form of logic flow diagrams.

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS
COMPUTATION OF REACTIVE CHEMICAL HAZARDS
REACTION SAFETY CALORIMETRY

CHEMICAL VAPOUR DEPOSITION (CVD)

Hammond, M. L., *Solid State Technol.*, 1980, **23**(12), 104–109

Hazards assodiated with the use of cleaning, etching and doping materials and procedures in semi-conductor CVD are codified, with 7 references.

See also GAS HANDLING

CHLORINATED PARAFFINS

Carbon black, Lead(IV) oxide, Manganese(IV) oxide

Chlorinated paraffins are viscous liquids or low-melting solids, depending on the chlorine content (40–80%) and the paraffin type. In general they are thermally unstable, tending to eliminate hydrogen chloride. In the absence of an inhibitor (usually a material which will react readily with traces of hydrogen chloride), they will soon turn brown or black at ambient temperature. Epoxides or glycols are often used as inhibitors at around 1% concentration, and chlorinated paraffins stabilised with propane-1,2-diol or epoxidised soya oil may be heated to 100°C with little change, though for limited periods, as the inhibitor becomes depleted with time.

DropBooks

See Lead(IV) oxide: Carbon black, etc.

See related HALOALKANES, HALOCARBONS

N-CHLORINATED PHOSPHORUS AMIDES $(RO)_2P(O)NCl_2$

Preparative hazard

See Chlorine: Dimethyl phosphoramidates

CHLORINATED POLY(DIMETHYLSILOXANES) $(-OSi(Me)(CH_2Cl)O-)_n$

Sosa, J. M., *Thermochim. Acta*, 1975, **13**, 100–104

Chlorinated silicone oil (DC200, with 15, 30 or 40% chlorine content; structure shown has 32%) decomposed violently on heating. Thermal stability decreased with increasing chlorine content and was investigated by TGA and DSC techniques.

CHLORINATED RUBBER

Metal oxides or hydroxides

1. Anon., *Chem. Trade J.*, 1962, **151**, 672
2. Anon., *Euro. Chem. News*, 1963, (May 24th), 29
3. 'Rept. GCS 27130', London, ICI, 1963
4. Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 12

Intimate mixtures of chlorinated rubber and zinc oxide or powdered zinc, with or without hydrocarbon or chlorinated solvents, react violently or explosively when heated at about 216°C. If in milling such mixtures local overheating occurs, a risk of a violent reaction exists. Such risks can be minimised by controlling milling temperatures, by cooling, or by using a mixture of maximum possible fluidity [1]. Similar reactions have been observed with antimony or lead oxides, or aluminium, barium or zinc hydroxides [2]. The full report [3] has been abstracted [4].

See related HALOALKENES

CHLORINE-CONTAINING SYSTEMS

1. Mal'tseva, A. S. *et al.*, *Chem. Abs.*, 1975, **82**, 45981
2. Dokter, T., *Explosion hazards of methyl chloride and chlorine-containing systems*, PhD thesis, Twente University, Netherlands. 1987
3. Gustin J-L., *Ind. Chem. Libr.*, 1996 **8** (Roots of Organic Development), 431, Elsevier

Explosive limits and hazards of various binary and ternary systems containing chlorine or its compounds are reviewed and discussed [1]. The safety aspects of operating a proposed pilot plant for the continuous production of dichloromethane and chloroform from chloromethane and chlorine have been studied in an explosion hazards analysis. The study has been augmented by experimental investigation of many of the safety parameters revealed in the study for which no results were available. Such parameters include flammability limits, burning velocities and quenching diameters, detonation limits and velocities, ignition energies and autoignition temperatures in the gaseous system chloromethane–dichloromethane–chlorine–hydrogen chloride; autoignition temperatures of chloromethane and dichloromethane in chlorine. Additionally, the formation of the highly explosive nitrogen trichloride during chlorination of materials containing ammonium salts or other nitrogen source was studied [2]. A review covering auto-ignition, deflagration and detonation of chlorination reactions has appeared more recently [3].

Chlorine drying towers

See Hydrogen: Oxygen, Sulfuric acid
See Chlorine

CHLORITE SALTS ClO_2^-

1. Mellor, 1941, Vol. 2, 284; 1956, Vol. 2, Suppl. II (Halogens), 573–575
2. Pascal, 1960, Vol. 16, 263

Many of the salts which have been prepared are explosive and sensitive to heat or impact. These include chlorites of copper (violent on impact), hydrazine (monochlorite, inflames when dry), nickel (explodes at 100°C but not on impact), silver (at 105° or on impact), sodium, tetramethylammonium, mercury, thallium and lead (which shows detonator properties). Several other chlorites not isolated and unstable in solution include mono-, di- and tri-methylammonium chlorites. The metal salts are powerful oxidants [1]. Chlorites are much less stable than the corresponding chlorates, and most will explode under shock or on heating to around 100°C [2]. Individually indexed compounds are:
Barium chlorite, 0204
Calcium chlorite, 3925
Hydrazinium chlorite, 4008
Lead(II) chlorite, 4102
Lithium chlorite, 4020
Mercury(I) chlorite, 4080
Mercury(II) chlorite, 4077
Methylammonium chlorite, 0500
Nickel chlorite, 4093
Potassium chlorite, 4016
Silver chlorite, 0010
Sodium chlorite, 4038
Tetramethylammonium chlorite, 1742
Thallium(I) chlorite, 4043
See also OXOSALTS OF NITROGENOUS BASES

DropBooks

CHLOROFLUOROCARBONS

RSC Lab. Hazard Data Sheet No. 75, 1988

Information is given on Freons 11, 12, 13, 21, 22. 113, 114: trichlorofluoro-, dichlorodifluoro-, chlorotrifluoro-, dichlorofluoro- and chlorodifluoro-methane; 1,1,2-trichloro-1,2,2-trifluoro-, and 1,2-dichloro-tetrafluoro-ethane, respectively.
See Chlorodifluoromethane
1,2-Dichlorotetrafluoroethane
Trichlorofluoromethane
See also HALOCARBONS

***N*-CHLORONITROAMINES** **$RN(Cl)NO_2$**

Grakauskas, V. *et al., J. Org. Chem.*, 1972, **37**, 334
N-Chloronitroamines and the derived *N*-chloro-*N*-nitrocarbamates are explosive compounds and decompose rapidly in storage.
See *N*-Fluoro-*N*-nitrobutylamine
See other *N*-HALOGEN COMPOUNDS, *N*-NITRO COMPOUNDS

CHLOROPHYLL

Ichimura, S. *et al.*, Japan Kokai, 74 86 512, 1974

Chlorophyl adsorbed on clay, or powdered unicellular green algae (chlorella) can be caused to explode by focussed irradiation from a powerful ruby laser.

See other IRRADIATION DECOMPOSITION INCIDENTS

CLATHROCHELATED METAL PERCHLORATES

Goedeken, V. L., *Inorg. Synth.*, 1980, **20**, 89

In the tris(2,3-butanedione dihydrazone) complexes of e.g. iron(II), nickel or cobalt(II or III) salts, the metal atom is effectively enclosed in an open ended chelating cylinder. The end of the cylinder can be closed by treating the complex with acidified aqueous formaldehyde, when at each end of the cylinder the 3 amino groups are converted to a hexahydrotriazine ring to give the clathrochelate salt. When the metal salts are perchlorates (and the formaldehyde is acidified with perchloric acid), the products must be regarded as treacherously unstable, like other perchlorate salts containing oxidisable matter, with avoidance of heating either the solids or the conc. solutions.

Individually indexed compounds are:
5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo [8.8.4.$1^{3,17}$.$1^{8,12}$]tetracosa-4,6,13,15,19,21-hexaene-N^4,N^7,N^{13},N^{16},N^{19},N^{22} cobalt(II) perchlorate, 3768
5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo [8.8.4.$1^{3,17}$.$1^{8,12}$]tetracosa-4,6,13,15,19,21-hexaene-N^4,N^7,N^{13},N^{16},N^{19},N^{22} iron(II) perchlorate, 3769
5,6,14,15,20,21-Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo [8.8.4.$1^{3,17}$.$1^{8,12}$]tetracosa-4,6,13,15,19,21-hexaene-N^4,N^7,N^{13},N^{16},N^{19},N^{22} nickel(II) perchlorate, 3770

See AMMINEMETAL OXOSALTS, [14] DIENE-N_4 COMPLEXES
POLYAZACAGED METAL PERCHLORATES
TETRAAZAMACROCYCLANEMETAL PERCHLORATES

CLEANING BATHS FOR GLASSWARE

Stahr, H. M. *et al.*, *Anal. Chem.*, 1982, **54**, 1456A

As a safer and cheaper alternative to the use of sulfuric acid–dichromate mixtures (chromic acid, and of the hazardous nitric acid–ethanol, or sulfuric acid–permanganate mixtures), a sulfuric acid–ammonium persulfate bath is recommended as long-lasting and economical. However, any such oxidant mixture should be used with caution, and only when necessary. In the absence of significant adherent residues on glassware, one of the proprietary detergent formulations should give adequate cleaning, except perhaps for the most rigorous surface chemistry or trace analysis requirements.

See Chromic acid
Nitric acid: Alcohols (reference 2), 4600

Nitric acid: Glassware, 4436
Potassium permanganate: Sulfuric acid, etc. (references 2,3), 4709
See also PLANT CLEANING INCIDENTS

COAL

1. Rigsby, L. S., *J. Coal Qual.*, 1983, **2**(2), 16–20
2. Grossman, S. L. *et al.*, *Coal Sci. Technol.* 1995, 24(Coal Sci. Vol. I), 469, 473.
3. Grossman, S. L. *et al., Erdöl, Erdgas, Köhle*, 1996, **112**(7/8), 322
4. Marzec, A., *Chem. Abs.*, 1997, **127**, 164191e

All aspects of self-heating of coal during storage and transportation are considered, and the main factors are identified as temperature, rank, particle size, moisture and pyrites contents [1]. Although explosions are always attributed to methane, in fact bituminous coal emits hydrogen during warm storage by an oxidative decomposition mechanism, which can be a danger if ventilation is poor [2,3,4].

Sodium carbonate
See AUTOIGNITION TEMPERATURE (reference 7)
See also SELF-HEATING AND IGNITION INCIDENTS

COMMERCIAL ORGANIC PEROXIDES **C–OO–**

1. Boyars, C., *AD Rept. No. 742770*, Richmond (Va.), USNTIS, 1972
2. Lee, P. R., *J. Appl. Chem.*, 1969, **19**, 345–351
3. Leleu, *Cahiers*, 1980, (99), 279
4. Gehrke, H., *Zentr. Arbeitsmed. Arbeitsschutz*, 1977, **27**, 7–10
5. Venable, E., *Chem. Eng. News*, 1982, **60**(42), 94
6. Stull, 1977, 21
7. Wagle, U. D. *et al., Safety in Polyethylene Plants*, 1978, **3**, 62–68
8. Nakagawa, S., *Chem. Abs.*, 1979, **91**, 210654
9. de Groot, J. J. *et al., Runaway Reactions*, 1981, Paper 3/V, 1–17
10. de Groot, J. J. *et al., Ind. Eng. Chem., Proc. Des. Dev.*, 1981, **20**, 131–138
11. Mohan, V. K. *et al., J. Haz. Mat.*, 1982, **5**, 197–220
12. Fisher A., Ger. Offen., 2 637 940, 1978
13. *NFPA 43B*, Quincy (Ma), Natl. Fire Prot. Assocn., 1986

This group of compounds is widely used in industry as a radical source for initiation of polymerisation. They are available from several manufacturers in a very wide range of formulations in various diluents to reduce operational hazards. These were classified into 6 hazard levels and of the many materials available, the first list below of 6 compounds (all dry and unformulated except for that suffixed *, which is water-wetted) were included in the highest risk category. This specified the material as being sensitive to friction or mechanical shock equivalent to the dissipation of 1 kg m or less of energy within the sample.

Existing and proposed methods of evaluating transportation hazards of organic peroxides exposed to impact, explosive shock or thermal surge stimuli were reviewed, and a hazard classification system proposed [1]. Commercial 2-butanone peroxide ('MEK peroxide') as a 40% solution in dimethyl phthalate was previously

PropBooks

thought to be safe in normal storage or transport situations, but several road- and rail-tanker explosion incidents showed evidence of detonation. Application of steady-state thermal explosion theory allowed the prediction of critical mass and induction period in relation to temperature in bulk storage. The critical mass seems likely to have been attained in some of the incidents [2]. MEK peroxide diluted with mixed phthalate–phosphate esters and mixed with powdered charcoal gave accelerated decomposition above 35–40°C, with thick fumes [3]. (Catalysis by trace metals in the charcoal seems a likely factor). This peroxide is also used as a hardener in on-site production of polyester–concrete structural elements, and a violent explosion occurred which was attributed to incorrect storage conditions [4]. MEK peroxide is, of course, also an oxidant and will ignite acetone or other combustibles on contact, and may lead to explosion [5]. The result of calculations of the exothermic potential from thermal decomposition of neat MEK peroxide ($Q = 218.5$ kJ/mol, 1.79 kJ/g, leading to adiabatic product gas temperature of 832°C and a peak pressure of 32 bar) is related to the effects of a catastrophic transportation incident involving 17 t of mixed peroxides initiated by a small MEK peroxide fire [6].

A method was developed for the large-scale testing of the decomposition characteristics of commercial peroxides held in closed vessels of 2–120 l capacity fitted with bursting disks and temperature/pressure recording facilities. The results on *tert*-butyl peroxypivalate and *tert*-butyl peroxy-2-ethylhexanoate suggest that adequate pressure relief vents can be designed based on a constant area per unit volume of container [7]. The course and rate of pressure development when 20 organic peroxides were heated in a new pressure vessel test appear to offer a better assessment of potential hazards and pressure-relief requirements [8]. Thermal phenomena involved in the self-heating decomposition processes of organic peroxides have been investigated under isothermal, adiabatic and temperature-scanning conditions. A new rapid test method had been developed for assessing the effect of impurities upon stability [9]. Both simulated and experimental investigations of worst probable hazards likely from exothermic decomposition of bulk tanks (10 m^3) of commercial organic peroxides are described, and emergency procedures formulated [10]. A range of 6 commercial organic peroxides and hydrogen peroxide was screened using a variety of tests and a simplified classification of peroxides into 3 groups is proposed [11]. The use of expanded sodium borate as a carrier for organic peroxides is claimed to improve resistance to fire and detonation, and allows their safe use as catalysts, especially in aqueous systems [12]. A recent US National Fire Code covers requirements for safe storage of commercial formulated mixtures [13].

Individually indexed commercial peroxides are:
Acetyl cyclohexanesulfonyl peroxide, 3033
Bis(3-carboxypropionyl) peroxide, 2990
Bis(2,4-dichlorobenzoyl) peroxide, 3623
Bis(2-hydroperoxy-2-butyl) peroxide, 3078
Bis(1-hydroperoxycyclohexyl) peroxide, 3553
O–*O*-*tert*-Butyl hydrogen monoperoxymaleate, 3015

Diisopropyl peroxydicarbonate, 3034
1-Hydroperoxy-1′-hydroxydicyclohexyl peroxide, 3555
2-Phenyl-2-propyl hydroperoxide, 1387
See CYCLIC PEROXIDES, RADICAL INITIATORS

COMPLEX ACETYLIDES $K_m[M(C{\equiv}C)_n]$

1. Bailar, 1973, Vol. 4, 810
2. Nast, R. *et al.*, *Chem. Ber.*, 1962, **95**, 1470–1483
3. Nast, R. *et al.*, *Z. Anorg. Chem.*, 1955, **279**, 146–156

The title salts, where M is Cr(III), Co(II or III), Cu(0 or I), Au(I), Fe(II or III), Mn(II or III), Ni(0 or II), Pd(0), Pt(0 or II) or Ag(I) are frequently explosive [1], several of the analogous sodium salts being similar. A series of dialkynylpalladates and -platinates [2] and a tetraalkynylnickelate [3] are pyrophoric, while other tetraalkynylnickelates are explosive [3]. Most react violently with water. Individually indexed compounds are:

(Many of the equivalent sodium salts are similar)
∗ Bis(trimethylphosphine)nickel(0)–acetylene complex, 3093
Potassium bis(phenylethynyl)palladate(2−), 3699
Potassium bis(phenylethynyl)platinate(2−), 3700
Potassium bis(propynyl)palladate, 2308
Potassium bis(propynyl)platinate, 2309
Potassium diethynylpalladate(2−), 1394
Potassium diethynylplatinate(2−), 1395
Potassium hexaethynylcobaltate(4−), 3446
Potassium hexaethynylmanganate(3−), 3448
Potassium tetraethynylnickelate(2−), 2896
Potassium tetraethynylnickelate(4−), 2897
Potassium tetrakis(propynyl)nickelate(4−), 3513
∗ Potassium tricarbonyltris(propynyl)molybdate(3−), 3471
Sodium hexakis(propynyl)ferrate(4−), 3759

See other ACETYLENIC COMPOUNDS

COMPLEX HYDRIDES $[MH_n],[EH_n]$

1. Gaylord, 1956
2. Semenenko, K. N. *et al.*, *Russ. Chem. Rev.*, 1973, 1–13
3. Ashby, E. C., *Rept. AD-A057764*, Richmond (Va.), NTIS, 1978
4. Ashby, E. C., *J. Organomet. Chem.*, 1980, **200**, 1–10

This group of highly reactive compounds includes several which have found extensive use in preparative chemistry [1]. Properties and reactions of several covalent tetrahydroborates have been reviewed [2]. Preparation and properties of several new hydrides are given which are of interest as high-energy fuels in propellant systems [3,4]. Individually indexed compounds are:

∗ Aluminium dichloride hydride diethyl etherate, 0061
Aluminium tetrahydroborate, 0058

DropBooks

Beryllium tetrahydroborate, 0157
Beryllium tetrahydroborate–trimethylamine, 1337
Bis(cyclopentadienyl)niobium tetrahydroborate, 3324
Bis(dimethylaminoborane)aluminium tetrahydroborate, 1795
Caesium hexahydroaluminate(3−), 0067
Caesium lithium tridecahydrononaborate, 0194
Calcium tetrahydroborate, 0158
Cerium(III) tetrahydroaluminate, 0089
Copper(I) tetrahydroaluminate, 0068
∗ Diammineboronium tetrahydroborate, 0167
Disodium tridecahydrononaborate(2−), 0195
Hafnium(IV) tetrahydroborate, 0182
Heptakis(dimethylamino)trialuminium triboron pentahydride, 3676
Lithium dihydrocuprate, 4271
Lithium pentahydrocuprate(4−), 4273
∗ Lithium tetradeuteroaluminate, 0069
Lithium tetrahydroaluminate, 0075
Lithium tetrahydroborate, 0145
Lithium tetrahydrogallate, 4407
Magnesium tetrahydroaluminate, 0085
Manganese(II) tetrahydroaluminate, 0086
Potassium hexahydroaluminate(3−), 0077
Potassium tetrahydrozincate, 4516
Potassium trihydomagnesate
Silver hexahydrohexaborate(2−), 0027
Sodium dihydrobis(2-methoxyethoxy)aluminate, 2575
Sodium tetradecahydrononaborate, 0196
Sodium octahydrotriborate, 0177
Sodium tetrahydroaluminate, 0076
Sodium tetrahydroborate, 0147
Sodium tetrahydrogallate, 4408
∗ Tricyclopentadienyluranium tetrahydroaluminate, 3688
Uranium(III) tetrahydroborate, 0178
Uranium(IV) tetrahydroborate etherates, 0183
Zirconium(IV) tetrahydroborate, 0184

See other REDUCANTS *See also* METAL HYDRIDES, NON-METAL HYDRIDES

COMPRESSED GASES

1. Crowl, D. A. *Plant/Oper. Progr.* 1992, **11**(2), 47

Since the whole theme of this book is concerned with unexpected or concealed sources of energy, it is relevant to reiterate that compressed gases may contain a large content of kinetic energy over and above that potentially available from chemical reaction energy possibilities for the gas. A procedure for calculating available kinetic energy from rupture of compressed gas containers is found in

[1]. Compression heating, or just pressure, may explode many unstable gases, or combustible mixtures thereof, during only slight compression.
See GAS CYLINDERS

COMPUTATION OF REACTIVE CHEMICAL HAZARDS

1. Treweek, D. N. *et al., J. Haz. Mat.*, 1976, **1**, 173–189
2. Domalski, E. S. *et al., Proc. 4th Int. Symp. Transp. Haz. Cargoes*, 1975, USNTIS PB 254214
3. *CHETAH, Chemical Thermodynamic and Energy Release Evaluation Program*, Philadelphia, ASTM, 1975
4. Sherwood, R. M., *Chem. Brit.*, 1975, **11**, 417
5. Treweek, D. N. *et al., Ohio J. Sci.*, 1980, **80**(4), 160–166
6. Yoshida, T. *et al., Chem. Abs.*, 1981, **95**, 64605
7. Yoshida, T. *et al., Primary Evaluation of Incompatibility and Energy Release* in *Proc. 4th Symp. Chem. Problems. Conn. Stab. Explosives*, (Hansson, J., Ed.), Tokyo, 1976
8. Yoshida, T. *et al., Chem. Abs.*, 1983, **95**, 7923
9. Yoshida, T. *et al., Chem. Abs.*, 1982, **93**, 188632
10. Davies, C. A.. *et al.*, in *Chem. Process Haz. Rev.*, (Hoffmann, J. M. & Mason, D. C., eds.), ACS Symp. Ser. 274, Ch. 9, 81–90, 1985
11. Frurip, D. J. *et al., Plant/Oper. Progr.*.,1989, **8**(2), 100–104
12. Shanley, E. S. *et al., J Loss Prev. Process Ind.*, 1995, **8**(5), 261
13. Harrison, B. K., private communication, 1998

During past decades, several computational methods for predicting instability (or 'self-reactivity') and mutual reactivity ('other chemical reactivity') have been developed and tested. These have been variously based on structural and calculated thermodynamic parameters, amplified in some cases with experimentally determined data, to produce hazard rating systems.

These methods were jointly evaluated for their ability to predict successfully instability in a range of compound types. It was concluded that the relationship between the parameters considered and chemical stability was too obtuse for conventional statistical analysis. However, application of pattern-recognition techniques to statistical analysis was more fruitful, and 13 of the more promising parameters were evaluated successfully. Total under- and over-estimation error was below 10% relative to generally accepted forms of consensus grading into the 3 stability categories of explosive, hazardous decomposition or polymerisation, and non-hazardous. The methods appear to have great potential in minimising hazards in storage, transfer and transportation of chemicals [1].

In an alternative assessment of the effectiveness of these computer programs, it was concluded that explosive power was over-emphasised in relation to the more practically important aspect of sensitivity to initiation, and many compounds were being indicated as hazardous when they were not. There was also no provision for considering polymerisation as a hazardous possibility, and there was little quantitative data on this. The parameter best correlating with material sensitivity is the bond-dissociation energy. It was recommended that regulations specifying the

handling and transport of chemicals should be based on the concept of known self-reactivity of functional groups present (nitro, nitramine, peroxide, azide, etc.) [2].

One of the computer programs [3] is relatively simple to apply, and gives estimates of the maximum energy release possible for any covalent compound or mixture of compounds containing C, H, O, N, and up to 18 other specified elements. Reactions and products may be specified if known, but the only essential input from the user is the amount and structure of each compound involved, the latter expressed in terms of the number of standard groups or skeletal fragments present in the structure. The graded results serve as a screening guide to permit decisions on which reaction systems need more detailed and/or experimental investigation [4]. In view of the difficulties which attend the use of thermodynamic parameters to try to predict mutual reactivity possibilities between pairs of compounds ('other chemical reactivity'), a computational method has been developed which combines two existing reactivity-ranking procedures (NAS hazard rating system, and Lewis acid–base rating) which gives results within a 10% error margin of the experimental results of the Dow binary hazard classification system (measurement of exotherm and gas evolution on mixing two typical components). It is intended to incorporate this refinement into the CHETAH program [5]. The early program was used fairly successfully to correlate the calculated maximum heat of decomposition for various types of explosive materials (nitrate esters, nitramines, nitroaromatics, formulated explosives, and organic peroxides) with their performance in various standard tests and the heat of decomposition determined by sealed-cell DSC. Correlation was fairly good across the range of comparisons [6].

The EITP (Evaluation of Incompatibility from Thermodynamic Properties) program was originally applied to reduce the possibilities of fires occurring in chemical stores situated in earthquake zones, through collapse of shelving and indiscriminate mixing of reactive chemicals from broken containers. The program calculates for mixtures of 2 or more chemicals the maximum reaction heat (MRH) which is possible, and the proportions necessary for this. Working from case histories of incidents it was then possible to set threshold values for MRH below which no ignition was likely, so that storage schedules to segregate any potentially reactive chemicals could be prepared and implemented [7]. A second revised version (REITP2) was prepared and evaluated against the results of various instrumental tests for purposes more closely related to specific chemical stability problems in explosives and chemical intermediates and products [8]. The REITP program is effective for initial estimation of the degree of hazard arising from decomposition of unstable materials, while the sealed-cell DSC procedure gives more detail on the course and likely consequences of decomposition [9].

A general account of how the CHETAH program may be applied to estimation of chemical hazards in relation to process research and development has been given [10]. Progressively enhanced and user-friendly versions of CHETAH, which give an overall hazard assessment and are capable of running on personal computers are available from ASTM [11]. Comments critical of the criteria used for hazard evaluation in the 1994 CHETAH program [12] led to amendments and enhancements incorporated in the 1998 Windows version. The pure compound physical properties databank has since been expanded from 400 to 1500 compounds and the

number of structural Benson groups used in thermodynamic calculations to >730. An additional criterion, the Calculated Maximum Adiabatic Reaction Temperature (CART) is incorporated. Input of drawn structures via the CHEMDRAW package, with automatic subsequent calculations, is imminent. The new Windows version 7.3 is expected in 1999 [13].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS
CHEMICAL STABILITY/REACTIVITY ASSESSMENT
EXOTHERMICITY
EXPLOSIBILITY (references 3–5)
MAXIMUM REACTION HEAT

CONDUCTING POLYMERS

See PERCHLORATE-DOPED CONDUCTING POLYMERS

COOL FLAMES

1. Coffee, R. D., *Cool Flames*, Chapter 18, 323–338 in *Safety and Accident Prevention in Chemical Operations*, Fawcett, H. H. & Wood, W. S., (Eds.), New York, Wiley, 2nd edn., 1982
2. D'Onofrio, E. J., *Loss. Prev.*, 1980, **13**, 99–95
3. Kolodner, H. J. *et al., Proc. 3rd Intl. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 2, 345–355, SSCI, Basle, 1980
4. Baronnet, R. *et al., Oxid. Commun.*, 1983, **4**(1–4), 83–95
5. Coffee, R. D., *Loss Prev. Bull.*, 1988, (081), 19–23

DropBooks

The complex and incompletely understood phenomena of cool flames and their close relationship with autoignition processes is discussed in considerable detail. As the temperature of mixtures of organic vapours with air is raised, the rate of autoxidation (hydroperoxide formation) will increase, and some substances under some circumstances of heating rate, concentration and pressure will generate cool flames at up to 200°C or more below their normally determined AIT. Cool flames (peroxide decomposition processes) are normally only visible in the dark, are of low temperature and not in themselves hazardous. However, quite small changes in thermal flux, pressure, or composition may cause transition to hot flame conditions, usually after some delay, and normal ignition will then occur if the composition of the mixture is within the flammable limits.

Conditions most conducive to transition from cool flame to hot ignition are those encountered during sudden loss of vacuum and ingress of air during (or soon after) high temperature vacuum distillation processes. Many of the unexplained cases of ignition during these or similar processing operations of organic materials may be attributable to this transition [1]. In a study of the relationships of cool flame temperature, autoignition temperature and ignition delay times of a series of glycols in several sizes of containing vessels, it was found that ethylene glycol shows extremely long delay times. The transition from cool flame to hot ignition was demonstrated experimentally under conditions simulating progressive vacuum failure during vacuum distillation [2]. The same phenomenon, observed when air was admitted during vacuum distillation of a mixture of triethylene glycol

diacetate with 36% of acetic acid, was investigated experimentally prior to pilot scale preparation of the ester, when nitrogen rather than air was admitted to break vacuum [3]. A semi-empirical correlation between cool flame behaviour of an organic compound and structure has been developed, but further experimental work is necessary [4]. A brief account of the nature and significance of cool flames in relation to process safety is presented [5].

For an example, *See* †2,2-Dimethoxypropane, 1895

See AUTOXIDATION, AUTOIGNITION INCIDENTS

COOLING BATHS

Anon., *Sichere Chemiearbeit*, 1992, **44**(6), 70; *Jahresbericht*, 1991, 72

A substantial explosion, followed by a fire causing fatal burns to the experimenter, occurred when working with butyllithium in tetrahydrofuran cooled by a propan-2-ol/solid carbon dioxide freezing bath. It was considered that the explosion might have been fueled by isopropanol vapour in air. This explanation was rejected since the alcohol should have been below its flash point. However, making up such cooling baths, containing flammable solvents, does disperse considerable quantities of vapour and mist before the mix is fully cooled. There is a period of potential hazard, as there may be when the bath warms above the flash point once more.

COPPER CHROMITE CATALYST $Cu_2O.Cr_2O_3$

Alcohols

Budniak, H., *Chem. Abs.*, 1975, **83**, 134493

Copper chromite catalyst, after use in high-pressure hydrogenation of fatty acids to alcohols, is pyrophoric, possibly owing to presence of some metallic copper and/or chromium. Separation of the catalyst from the product alcohols at 130°C in a non-inerted centrifuge led to a rapid exotherm and autoignition at 263°C.

Ammonium perchlorate

See Ammonium perchlorate: Catalysts (reference 2)

See other HYDROGENATION CATALYSTS

CORROSION INCIDENTS

1. Hammer, N. E., *Dangerous Prop. Ind. Mater. Rept.*, 1981, **1**(8), 2–7
2. Asakura, S. *et al.*, *Chem. Abs.*, 1982, **96**, 147574
3. Maddison, T. E., *Loss Prev. Bull.*, 1987, (076), 31–38

Hazards created by corrosion involving consumer products, industrial installations, utility systems and dangerous wastes are reviewed [1]. Auto-accelerating corrosion reactions of copper components in acidic media which could lead to sudden plant failure have been studied [2]. Seven cases involving catastrophic failure of large glass-reinforced plastic (GRP) storage tanks are described, most stemming from corrosive attack of the GRP structural elements by the contained liquors, sometimes

after failure of a polymeric liner. Plastics are not commonly considered to be subject to corrosive attack [3].

Some examples of these incidents are:
Aluminium, : Butanol, 0048
Aluminium, : Mercury(II) salts, 0048
Aluminium, : Metal nitrates, Sulfur, Water, 0048
Aluminium, : Water, 0048
Ammonium sulfide, : Zinc, 4577
Calcium chloride, : Zinc, 3923
Chlorine, : Aluminium, 4047
Chlorine, : Steel, 4047
Gallium, : Aluminium alloys, 4406
Magnesium, : Methanol, 4690
Magnesium, : Halocarbons, 4690
Magnesium, : Water, 4690
Magnesium chloride, : Air, Mild steel, Water, 4081
Mercury, : Metals, 4600
Methacrylic acid, 1530
Orthophosphoric acid, : Chlorides, Stainless steel, 4505
Potassium, (references 4–5a), 4645
Sodium sulfide, : Glass, 4811
Uranium, : Nitric acid, Trichloroethylene, 4923

COTTON

DropBooks

Oils

Anon., *Textil-Rundschau*, 1957, **12**, 273
Cotton waste in contact with fatty oils (especially of unsaturated character) is much more subject to self-heating and autoignition than animal fibres. Various factors affecting storage hazards of baled cotton, including the aggravating effects of moisture, are discussed. Mineral oils, though generally less subject to oxidative heating than vegetable oils, have also been involved in autoignition incidents
See CELLULOSE

COUMARONE–INDENE RESIN

The finely powdered resin is a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)

CRITICAL IGNITION TEMPERATURE

Kotoyori, T., J. *Loss Prev. Proc. Ind.*, 1989, **2**, 16–21
Materials of limited thermal stability may self-heat and eventually ignite through progressive accelerating decomposition if they are stored or processed above the critical ignition temperature (CIT). Knowledge of this is therefore essential for

defining safe conditions for processing or storing such materials. Existing tests to determine this temperature involve a series of runs with adiabatic storage of samples at different (increasing) temperatures until ignition is observed. This temperature is not an absolute value, but depends on sample size and induction period allowed. In the BAM heat accumulation storage test, samples are the largest standard commercial package, amd the induction time is set at 7 days, the result being the self-accelerating decomposition temperature (SADT). Naturally, this test requires many kg of material to complete.

A new small-scale test has been developed which needs only a few g of thermally unstable material, which may be contained in an open cell version of the apparatus if aerobic processes are involved, otherwise in a closed cell apparatus, both with full temperature control and monitoring systems. Such materials may be divided into 2 types, depending on the behaviour of a sample after introduction into adiabatic storage at elevated temperature. The first type, which after attaining the adiabatic temperature shows a steady further increase in temperature in line with Frank-Kamenetski's thermal explosion theory, exhibit thermal combustion (TC) behaviour. In the second type, after adiabatic temperature has been reached, the sample shows a sudden rapid rate of rise, exhibiting autocatalytic (AC) behaviour as chain branching and acceleration set in. Of 8 materials examined in this test, five showed TC behaviour (azoisobutyronitrile, dibenzoyl peroxide, dinitrosopentamethylene tetramine, 4,4′-oxybis(benzenesulfonylhydrazide) and calcium hypochlorite), while 3 showed AC behaviour (cellulose nitrate, dilauroyl peroxide and toluenesulfonylhydrazide). CIT values, largely comparable with the BAM results, are given in the individual entries:

Azoisobutyronitrile, 3011
Calcium hypochlorite, 3924
Dibenzoyl peroxide, 3639
Didodecanoyl peroxide, 3857
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1954
4,4′-Oxybis(benzenesulfonylhydrazide), 3525
4-Toluenesulfonylhydrazide, 2827

See entries DEFLAGRATION INCIDENTS, HIGH RATE DECOMPOSITION

CROWN ETHERS

As cyclic polyethers (polyethylene oxides), some of this group of aprotic complexing solvents may be subject to peroxidation, though no reports have been so far noted.

See 1,4,7,10,13,16-Hexaoxacyclooctadecane ('18-Crown-6')

Bromoform, Potassium hydroxide, etc.

See Bromoform: Cyclic polyethylene oxides, Potassium hydroxide

1. Zabetakis, M. G., *Safety with Cryogenic Fluids*, London, Heywood, 1967
2. *Safety Panel, British Cryogenics Council, Cryogenics Safety Manual* – A Guide to Good Practice, Oxford, Butterworth-Heinemann, 3rd edn., 1991
3. *Safety Problems in Handling Low-Temperature Industrial Fluids*, 1964, IChE Symp. papers, published in *Chem. Engr.*, 1965, **43**(185), CE7–10; (186), CE36–48
4. Bernstein, J. T., *Cryogenics*, 1973, **13**, 600–602
5. *B.S. Code of Practice*, BS 5429: 1976
6. Timmerhaus, K. D. *et al., Adv. Cryog. Eng. 1977*, 1978, **23**, 721–729
7. *Recommended Safety Precautions for Handling Cryogenic Liquids*, Crawley, Edwards High Vacuum, 1979
8. Ordin, P. M., *Liqu. Cryog.*, 1983, **1**, 1–57
9. Hofmann, M. J., *J. Chem. Educ.*, 1986, **63**(6), A149–150
10. Ryan, K. P. *et al., Microscope*, (Oxford), 1987, **147**, 337–340
11. Rouault, F. C., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 537–556, Heidelberg, ISSA, 1987
12. Currie, J. L., *Cryogenics*, 1988, **28**, 830–834
13. Anon., *Sichere Chemiearbeit*, 1997, **49**(1), 10

The monograph presents concisely in 6 chapters the principles of safety applicable to cryogenics, with safety data sheets for 15 cryogenic fluids [1]. The revised safety manual covers the operation and maintenance of plant for producing, storing and handling commercial gases which liquefy at low temperatures, and precautions in the use of these materials [2]. The symposium covered possible fire and explosion hazards in general terms, as well as in detail for liquid hydrogen, acetylene, natural gas, and a low-temperature nitrogen-washing process for ammonia synthesis gas [3]. Safety aspects of sampling and handling cryogenic liquids were reviewed [4] and the Code of Practice provides users of liquid oxygen, nitrogen, argon, natural gas, etc. with a basic appreciation of the problems associated with the small-scale use and storage of these materials [5]. Aspects of cryogenic systems involving physiological materials and high pressure are discussed [6], and a 16-page booklet briefly covers essential aspects of the title topic [7]. The recent review of safety in handling and use of cryogenic fluids includes 69 references [8], and safe practices in their laboratory use are presented [9].

In a review of the use of various cryogenic liquids for rapid freezing of biological specimens for cryo-sectioning, hazards attendant on the use of liquid propane and similar cryogens are discussed. Upon evaporation, the volume of mixture with air within the explosive range may be 14,000 times that of the volume of original liquid, and this may be a significant proportion of the free space in a confined work area. Precautions including the use of nitrogen blanketing, a fume cupboard, and adequate ventilation are discussed [10]. The use of a computer controlled interlocked interactive sequencing system to prevent mistakes in loading road tankers with cryogenic liquids is described [11]. The role of the Cryogenics Safety Manual (reference 2 above) as a training guide is discussed, and the major changes in the scheduled 1988 revision are highlighted [12].

DropBooks

A cryogenic storage vial frozen in liquid nitrogen exploded on rewarming to just above ambient temperature, injuring a worker. It is considered that liquid nitrogen seeped round the contracted and hardened seal, which resealed on warming. It is suggested caps be loosened immediately on removal from storage and (impractically?) that vials be filled to the brim, leaving no room for liquid gases [13].

Some examples of cryogens are:

† Propane, 1271
Nitrogen (Liquid), 4735
Oxygen (Liquid), 4832
† Hydrogen (Liquid), 4454

See Argon, Liquid nitrogen

See also LIQUEFIED GASES

CRYSTALLINE HYDROGEN PEROXIDATES

1. Castrantas, 1965, 4
2. Emeléus, 1960, 432
3. Kirk-Othmer, 1966, Vol. 11, 395
4. Mellor, 1971, Vol. 8, Suppl. 3, 824
5. Editor's comments, 1999
6. Jones, D. P. *et al., J. Chem. Soc., Dalton Trans.*, 1980, 2526–2532

Many compounds will crystallise out with hydrogen peroxide in the crystal lattice, analogous to crystalline hydrates. A few (some of which are listed below) sequester the peroxide preferentially from water. These complexes represent a form of concentrated hydrogen peroxide distributed at a molecular level, which may react violently in close contact (grinding or heating) with oxidisable materials [1–4]. If the host is itself oxidisable, this molecular distribution makes detonability highly probable [5]. Some examples of true peroxodicarbonates (MOCO.OOCO.OM) have been prepared, but they do not behave as oxidants, immediately hydrolysing in water to hydrogen peroxide [6]. Individually indexed compounds are:

1,4-Diazabicyclo[2.2.2]octane hydrogen peroxidate, 2473
Potassium citrate tri(hydrogen peroxidate), 2258
Potassium fluoride hydrogen peroxidate, 4300
Sodium borate hydrogen peroxidate, 0154
Sodium carbonate hydrogen peroxidate, 0552
Sodium pyrophosphate hydrogen peroxidate, 4816
Triethylamine hydrogen peroxidate, 2570
Urea hydrogen peroxidate, 0476

See Hydrogen peroxide: Nitric acid, Thiourea

CUBANES $C_8H_{8-n}X_n$

1. Eaton, P. E., *Angew. Chem. (Int.)*, 1992, **31**(11), 1421
2. Eaton, P., *Chem. Abs*, 1993, **119**, 75812
3. Schmitt, R. J. *et al., Chem. Abs* . 1994, **121**, 112782
4. Piermarini, G. J. *et al., Propellants, Explos., Pyrotech., 1991,* **16**(4), 188

5. Su, Z. *et al., Proc. Int. Pyrotech. Semin.*, 1991, (17th) Vol. 1, 224
6. Eaton, P. E. *et al., J. Amer. Chem. Soc.*, 1997, **119**(41), 9591

All cubanes are high energy materials and should be handled with due precautions for potential explosives [1]. The ring system has almost 700 kJ/mol strain energy (more, per unit weight, than the detonation energy of TNT) and is under study as a basis for high power explosives [2,3]. Cubane itself explodes spontaneously at 3 GPa pressure, the 1,4-dinitro derivative not until >7 GPa [4]. The slightly less strained homocubanes are also studied as explosives [5]. Cubane acyl azides are sensitive and powerful primary explosives; they should be handled only in dilute solution [6]. Individual cubanes are:

1,4-Dinitropentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane, 2918

Pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane, 2942

Pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane-1,2-dicarboxylic acid, 3261

See other STRAINED-RING COMPOUNDS

CYANIDES CN$^-$

Hypochlorites

1. Wallace, V., *Chem. Eng. News*, 1978, **56**(4), 3
2. Kirk-Othmer, 3rd Edn., Vol. 7, 322

Care is necessary in using hypochlorite solutions to destroy cyanide wastes by oxidation to cyanates. This reaction goes readily, even at high pH, but the secondary oxidation of cyanate to nitrogen and carbon dioxide is very pH dependent. This is slow at pH 11 but runs away at 10−10.3, with subsequent sudden release of nitrogen gas. Disposal operations should be conducted to avoid the combination of high pH, excess of hypochlorite and moderate or high concentrations [1]. On the other hand, pH above 9 is recommended to avoid nitrogen trichloride formation [2]. Addition of 0.5 ml of cyanide solution to 5 ml of stirred hypochlorite destroyed a gas meter with the violent gas evolution [1].

See Nitrogen trichloride

See other GAS EVOLUTION INCIDENTS

See METAL CYANIDES (AND CYANO COMPLEXES)

CYANO COMPOUNDS -C≡N, C≡N$^-$

Metal cyanides are readily oxidised and those of some heavy metals show thermal instability. The covalent cyano group is endothermic, and hydrogen cyanide and many organic nitriles are unusually reactive under appropriate circumstances, and *N*-cyano derivatives are reactive or unstable. The class includes the groups:

3-CYANOTRIAZENES, METAL CYANIDES (AND CYANO COMPLEXES)
DIISOCYANIDE LIGANDS

Individually indexed compounds are:

† Acetonitrile, 0758
† Acrylonitrile, 1107
∗ Allyl isothiocyanate, 1471

DropBooks

3-Aminopropiononitrile, 1212
∗ Ammonium thiocyanate, 0479
Azidoacetonitrile, 0714
2,2′-Azobis(2,4-dimethylvaleronitrile), 3668
Azoisobutyronitrile, 3011
2,2′-Azoisovaleronitrile, 3345
Bis(acrylonitrile)nickel(0), 2312
Bis(2-cyanoethyl)amine, 2397
∗ 1,3-Bis(isocyanomethyl)benzene, 3257
∗ Bis(trifluoromethyl)cyanophosphine, 1053
∗ Butane-1,4-diisocyanate, 2376
† Butyl isocyanate, 1931
† Butyronitrile, 1563
Caesium cyanotridecahydrodecaborate(2−), 0518
Calcium cyanamide, 0316
2-Carbamoyl-2-nitroacetonitrile, 1116
∗ Carbonyl diisothiocyanate, 1342
† 2-Chloroacrylonitrile, 1074
2-Chlorobenzylidenemalononitrile, 3333
4-Chlorobutyronitrile, 1487
2-Chloro-1-cyanoethanol, 1130
∗ 4-Chlorophenyl isocyanate, 2648
∗ Chlorosulfonyl isocyanate, 0324
Cyanamide, 0404
Cyanoacetic acid, 1113
Cyanoacetyl chloride, 1075
∗ Cyanoborane oligomer, 0393
N-Cyano-2-bromoethylcyclohexylamine, 3178
Cyanocyclopropane, 1463
Cyanodiazoacetyl azide, 1346
2-Cyanoethanol (3-Hydroxypropanenitrile), 1181
Cyanoform, 1383
Cyanoformyl chloride, 0600
Cyanogen bromide, 0313
Cyanogen chloride, 0323
Cyanogen fluoride, 0323
Cyanoguanidine, 0813
Cyanohydrazonoacetyl azide, 1083
∗ Cyanonitrene, 0540
2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2668
4-Cyano-3-nitrotoluene, 2917
3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-)oxide, 2630
2-Cyano-2-propanol, 1566
† 1-Cyanopropene, 1464
† 3-Cyanopropene, 1465
1-Cyano-2-propen-1-ol, 1467

2-Cyano-2-propyl nitrate, 1506
∗ 3-Cyanopropyne, 1416
† Cyanotrimethylsilane, 1665
2-Cyano-1,2,3-tris(difluoroamino)propane, 1432
Diazidomalononitrile, 1347
Diazidomethylenecyanamide, 1017
2,3-Diazidopropiononitrile, 1121
Diazomalononitrile, 1344
2-Diazonio-4,5-dicyanoimidazolide, 2050
∗ 1,2-Dibromo-1,2-diisocyanatoethane polymers, 3165
∗ Dibutylthallium isocyanate, 3193
† Dicyanoacetylene, 1801
1,4-Dicyano-2-butene, 2311
Dicyanodiazene, 1005
Dicyanofurazan, 1803
Dicyanofurazan *N*-oxide, 1804
† Dicyanogen, 0996
∗ Dicyanogen *N,N′*-dioxide, 0998
Dicyanoiodonium triflate, 1048
(Difluoroamino)difluoroacetonitrile, 0630
∗ 1,6-Diisocyanatohexane, 3008
∗ Diisocyanatomethane, 1079
∗ 2,4-Diisocyanatotoluene, 3117
∗ 1,4-Diisocyanobutane, 2372
∗ 1,5-Diisocyanopentane, 2825
∗ Disodium dicyanodiazenide, 1006
∗ Disulfur thiocyanate, 1003
∗ 3-Ethoxycarbonyl-4,4,5,5-tetracyano-3-trimethylplumbyl-4,
5-dihydro-3*H*-pyrazole, 3611
Ethyl cyanoacetate, 1889
Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate, 2359
∗ Ethyl isocyanide, 1178
Fumarodinitrile, 1397
∗ Germanium isocyanate, 1377
Glutarodinitrile, 1870
Glycolonitrile, 0760
∗ Hexaethyltrialuminium trithiocyanate, 3695
Hydrogen Cyanide, 0380
† Isobutyronitrile, 1565
∗ Isocyanoamide, 0407
∗ 2-Isocyanoethyl benzenesulfonate, 3143
∗ Isopropylisocyanide dichloride, 1561
Malononitrile, 1078
Mercaptoacetonitrile, 0767
Methyl 3,3-diazido-2-cyanoacrylate, 1824
† Methyl isocyanate, 0761

DropBooks

∗ Methyl isocyanide, 0759
∗ Methyl isocyanoacetate, 1470
∗ 1-Naphthyl isocyanate, 3390
2-Nitrobenzonitrile, 2662
Nitrosyl cyanide, 0541
∗ Oxopropanedinitrile, 1341
Perfluoro-*N*-cyanodiaminomethane, 0637
Phenylacetonitrile, 2935
2,2′-[1,4-Phenylenebis(azidomethylidyne)]bis(propanedinitrile), 3622
∗ 2-Phenylethyl isocyanate, 3139
∗ Phosphorus tricyanide, 1343
∗ Phosphoryl dichloride isocyanate, 0327
† Pivalonitrile, 1929
† Propiononitrile, 1179
Silver 3-cyano-1-phenyltriazen-3-ide, 2670
Succinodinitrile, 1433
Sulfinylcyanamide, 0542
∗ Sulfur thiocyanate, 1002
∗ Tetraacrylonitrilecopper(I) perchlorate, 3510
Tetracyanoethylene, 2629
Tetracyanooctaethyltetragold, 3814
Tetramethylsuccinodinitrile, 3007
∗ Thiocarbonyl azide thiocyanate, 1011
∗ Thiocyanogen, 1001
Trichloroacetonitrile, 0607
Trinitroacetonitrile, 1009
∗ Vinyl isocyanide, 1109

3-CYANOTRIAZENES **N═N−N(C≡N)**

Bretschneider, H. *et al., Monatsh.*, 1950, **81**, 981
Many aromatic 3-cyanotriazenes are shock-sensitive, explosive compounds.
See other HIGH-NITROGEN COMPOUNDS, TRIAZENES

CYCLIC PEROXIDES

1. Swern, 1970, Vol. 1, 37; 1972, Vol. 3, 67, 81
2. Nixon, J. R. *et al., J. Org. Chem.*, 1978, **43**, 4052, footnote 18

Generally produced *inter alia* during peroxidation of aldehydes or ketones, the lower members are often violently explosive. Dimeric and trimeric ketone peroxides are the most dangerous group of organic peroxide, exploding on heating, touching or friction [1]. Some bromo- and hydrido-cyclic peroxides exploded repeatedly during microanalytical combustion [2]. Individually indexed compounds are:
2,2′-Biphenyldicarbonyl peroxide, 3631
1,6-Diaza-3,4,8,9,12,13-hexaoxabicyclo[4.4.4]tetradecane, 2476

2,3-Dibromo-5,6-epoxy-7,8-dioxabicyclo[2.2.2]octane, 2298
3,6-Dichloro-3,6-dimethyltetraoxane, 1492
4,5-Dichloro-3,3,4,5,6,6-hexafluoro-1,2-dioxane, 1355
2,3:5,6-Diepoxy-7,8-dioxabicyclo[2.2.2]octane, 2339
3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane, 3052
2,5-Dimethyl-2,5-dihydrothiophene-2,5-endoperoxide, 2387
Dimethyldioxirane, 1227
3,6-Dimethyl-1,2,4,5-tetraoxane, 1625
1,4-Dimethyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene, 2388
7,8-Dioxabicyclo[4.2.2]-2,4,7-decatriene, 2955
cis-1,4-Dioxenedioxetane, 1538
3,6-Dioxo-1,2-dioxane, 1445
3,6-Di(spirocyclohexane)-1,2,4,5-tetraoxane, 3546
1,6-Di(4′-tolyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3796
9,10-Epidioxyanthracene, 3630
1,4-Epidioxy-1,4-dihydro-6,6-dimethylfulvene, 2984
1,4-Epidioxy-2-*p*-menthene, 3347
endo-2,3-Epoxy-7,8-dioxabicyclo[2.2.2]oct-5-ene, 2336
3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane, 3195
3- or 4-Methoxy-5,6-benzo-6*H*-1,2-dioxin, 3154
3-Methoxy-3-methyl-5,6-benzo-6*H*-1,2-dioxin, 3313
3-Methoxy-4-methyl-5,6-benzo-6*H*-1,2-dioxin, 3314
1-(*cis*-Methoxyvinyl)-1,4-endoperoxy-2,5-cyclohexadiene, 3153
Methyltrifluoromethyldioxirane, 1102
3-Methyl-1,2,4-trioxolane, 1235
4a,8a,9a,10a-Tetraaza-2,3,6,7-tetraoxaperhydroanthracene, 2478
3,3,4,5-Tetrachloro-3,6-dihydro-1,2-dioxin, 1390
3,3,6,6-Tetrakis(bromomethyl)-9,9-dimethyl-1,2,4,5,7,8-hexoxonane, 3173
Tetramethyl-1,2-dioxetane, 2508
3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane, 2517
7,7,10,10-Tetramethyl-1,2,5,6-tetroxecane-3,4-dione, 3349
3,6,9-Triethyl-1,2,4,5,7,8-hexoxonane, 3196
Tri(spirocyclopentane)1,1,4,4,7,7-hexoxonane, 3693
See Hydrogen peroxide: Ketones, Nitric acid
See also COMMERCIAL ORGANIC PEROXIDES, DIOXETANES

DropBooks

DEFLAGRATION INCIDENTS

See entries CRITICAL IGNITION TEMPERATURE, PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION(reference 3)

Some incidents involving deflagration may be found under:
Ammonium dichromate
4-Chloronitrobenzene
1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene
Hydroxylaminium sulfate

4-Nitrobenzoic acid
2-Nitrosophenol (1,2-Benzoquinone monoxime)
Sodium 3-nitrobenzenesulfonate

DEFLAGRATION TO DETONATION

Chatrathi, K. *et al.*, *Process Safety Progr.*, 1996, **15**(4), 237

A study of deflagration to detonation transition in pipes, for gas/air and dust mixtures, has been made and reported. Obviously it depends upon the exact mixture, but departures from the straight and narrow generally facilitate this transition from slight to seriously destructive over-pressures.

See also DUST EXPLOSION INCIDENTS, GEOMETRY OF VESSELS AND PIPEWORK, VAPOUR CLOUD EXPLOSIONS

DEVARDA'S ALLOY **Cu−Al−Zn**

1. Cameron, W. G., *Chem. & Ind.*, 1948, 158
2. Chaudhuri, B. B., *Chem. & Ind.*, 1948, 462

The analytical use of the alloy to reduce nitrates is usually accompanied by the risk of a hydrogen explosion, particularly if heating is effected by flame. Use of a safety screen and flameless heating, coupled with displacement of hydrogen by an inert gas, are recommended precautions [1]. The explosion was later attributed to gas pressure in a restricted system [2].

See other ALLOYS, GAS EVOLUTION INCIDENTS

DIACYL PEROXIDES **RCO.OOCO.R, RSO_2.OOSO.R_2**

1. Swern, 1970, Vol. 1, 70
2. Mageli, O. L. *et al.*, US Pat. 3 956 396, 1976
3. Fujimori, K., *Org. Peroxides, Chichester, John Wiley*, 1992, 319

Most of the isolated diacyl (including sulfonyl) peroxides are solids with relatively low decomposition temperatures, and are explosive, sensitive to shock, heat or friction. Several, particularly the lower members, will detonate on the slightest disturbance. Autocatalytic (self-accelerating) decomposition, which is promoted by tertiary amines, is involved [1]. Solvents suitable for preparation of safe solutions of diacetyl, dipropionyl, diisobutyryl and di-2-phenylpropionyl peroxides are disclosed [2]. The class is reviewed, including hazards and safety measures [3]. Cyclic diacyl peroxides are more stable, but scarcely to be trusted. Individually indexed compounds are:

Acetyl cyclohexanesulfonyl peroxide, 3033
2,2′-Biphenyldicarbonyl peroxide, 3631
∗ Bis(2-azidobenzoyl) peroxide, 3628
Bis(bromobenzenesulfonyl) peroxide, 3453
Bis(3-carboxypropionyl) peroxide, 2990
Bis(4-chlorobenzenesulfonyl) peroxide, 3458
Bis(3,4-dichlorobenzenesulfonyl) peroxide, 3445
Bis(2,4-dichlorobenzoyl) peroxide, 3623

Bis(fluoroformyl) peroxide, 0625
Bis-3-(2-furyl)acryloyl peroxide, 3640
Bis(trichloroacetyl) peroxide, 1361
Bis(trifluoroacetyl) peroxide, 1367
Diacetyl peroxide, 1537
Dibenzenesulfonyl peroxide, 3499
Dibenzoyl peroxide, 3639
Di-3-camphoroyl peroxide, 3807
Dicrotonoyl peroxide, 2986
Dicyclohexylcarbonyl peroxide, 3667
Didodecanoyl peroxide, 3857
Di-2-furoyl peroxide, 3245
Dihexanoyl peroxide, 3554
Diisobutyryl peroxide, 3032
Diisopropyl peroxydicarbonate, 3034
Dimethanesulfonyl peroxide, 0931
Di-2-methylbutyryl peroxide, 3354
Di-1-naphthoyl peroxide, 3831
3,6-Dioxo-1,2-dioxane, 1445
Dipropionyl peroxide, 2442
Dipropyl peroxydicarbonate, 3035
Di-4-toluenesulfonyl peroxide, 3656
Peroxodisulfuryl difluoride, 4328
Phthaloyl peroxide, 2900
Potassium benzenesulfonylperoxosulfate, 2257
Potassium *O*–*O*-benzoylmonoperoxosulfate, 2684
∗ *O*-Trifluoroacetyl-*S*-fluoroformyl thioperoxide, 1050
See PEROXIDES, PEROXYCARBONATE ESTERS

DropBooks

DIALKYL HYPONITRITES **RON=NOR**

1. Partington, J. R. *et al., J. Chem. Soc.*, 1932, **135**, 2593
2. Mendenhall, G. D. *et al., J. Amer. Chem. Soc.*, 1982, **104**, 5113
3. Ogle, C. A. *et al., J. Org. Chem.*, 1983, **48**, 3728–3733

The violence of the explosion when the ethyl ester was heated at 80°C was not so great as reported previously. The propyl and butyl esters explode if heated rapidly, but decompose smoothly if heated gradually [1]. Dialkyl hyponitrites with alkyl groups below C_6 are shock-sensitive [2]. The shock-sensitivity decreases with increasing MW, and it was not possible to detonate esters above C_6. The aryl esters were insensitive and the alkyl esters became so on dilution with solvent [3].
Individually indexed compounds are:
Dibutyl hyponitrite, 3069
trans-Di-*tert*-butyl hyponitrite, 3070
Diethyl hyponitrite, 1690
Diisopropyl hyponitrite, 2538
Dimethyl hyponitrite, 0913

Dipropyl hyponitrite, 2539
See related AZO COMPOUNDS

DIALKYLMAGNESIUMS **R_2Mg**

Alcohols, Ammonia, Carbon dioxide or Water
Sidgwick, 1950, 233
This series, either as the free alkyls or their ether complexes, is extremely reactive, igniting in air or carbon dioxide and reacting violently or explosively with alcohols, ammonia or water. Individually indexed compounds are:
Diethylmagnesium, 1687
Dimethylmagnesium, 0908
Diphenylmagnesium, 3482
See other ALKYLMETALS

DIALKYL PEROXIDES **ROOR**

1. Castrantas, 1965, 12
2. Swern, 1970, 1, 38, 54
3. Davies, 1961, 75
4. Uetake, K. *et al., Bull. Chem. Soc. Japan*, 1979, **52**, 2136

The high and explosive instability of the lower dialkyl peroxides decreases rapidly with increasing chain length and degree of branching, the di-*tert*-alkyl peroxides being amongst the most stable of the group [1,2]. Though many 1,1-bis(peroxides) have been reported, few have been purified because of the higher explosion hazards, compared with the monofunctional peroxides [3]. Samples of 4 pure liquid dialkyl peroxides were thermally decomposed in TGA–DSC equipment to provide information for hazard prevention [4]. Individually indexed compounds are:

∗ Bis(2-hydroperoxy-4-methyl-2-pentyl) peroxide, 3566
2-(4-Bromophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3709
2-(4-Chlorophenyl)-2-propyl 1-(1,1-dimethyl-2-pentyn-4-enyl) peroxide, 3711
† Di-*tert*-butyl peroxide, 3074
∗ 2,2-Di(*tert*-butylperoxy)butane, 3565
Diethyl peroxide, 1699
Dimethyl peroxide, 0923
Dipropyl peroxide, 2547
Ethyl methyl peroxide, 1282

See PEROXIDES

DIALKYLZINCS **R_2Zn**

1. Sidgwick, 1950, 266
2. Noller, C. R., *J. Amer. Chem. Soc.*, 1929, **51**, 597
3. Houben-Weyl, 1973, Vol. 13.2a, 560, 576

The dialkylzincs up to the dibutyl derivatives readily ignite and burn in air. The higher alkyls fume but do not always ignite [1]. During preparation of dialkylzincs,

reaction of the copper–zinc alloy with mixed alkyl bromides and iodides must begin (exotherm, often after a long induction period), before too much halide mixture is added, or violent explosions may occur [2]. Reactions with water may be explosive [3].
See other INDUCTION PERIOD INCIDENTS

Acyl halides
Houben-Weyl, 1973, Vol. 13.2a, 781
Too-fast addition of acyl halides during preparation of ketones may lead to explosive reactions.

Alkyl chlorides
Noller, C. R., *J. Amer. Chem. Soc.*, 1929, **51**, 599
During interaction to give hydrocarbons, too much chloride must not be added before reaction sets in (induction period), or explosions may occur.
See other INDUCTION PERIOD INCIDENTS

Methanol
Houben-Weyl, 1973, Vol. 13.2a, 855
Contact of the neat liquids with uncooled methanol is explosively violent and leads to ignition. For analysis, ampouled samples of dialkylzincs must first be frozen in liquid nitrogen before being broken under methanol–heptane mixtures at −60°C.
See Zinc ethoxide: Nitric acid

Individually indexed compounds are:
Dibutylzinc, 3080
Diethylzinc, 1718
Diisobutylzinc, 3081
Diisopentylzinc, 3371
Dimethylzinc, 0935
Dipropylzinc, 2551
See other ALKYLMETALS

DropBooks

1,3-DIAZA-2-BORACYCLOALKANES

Alcohols
Merriman, J. S. *et al., Inorg. Synth.*, 1977, **17**, 165
These heterocycles react readily with protic solvents, and alcohols in particular may occasionally cause explosive solvolysis reactions.
See related BORANES

DIAZIRINES

1. Schmitz, E. *et al., Org. Synth.*, 1965, **45**, 85
2. Liu, M. T. H., *Chem. Eng. News*, 1974, **52**(36), 3
3. Terpinski, J. *et al., Magn. Reson. Chem.*, 1987, **25**, 923–927

Diazirine and several of its 3-substituted homologues, formally cyclic azo compounds, are explosive on heating or impact [1]. The shock-sensitivity of all diazirine compounds and the inadvisability of their handling in the undiluted state have again been stressed [2]. In a description of the synthesis of 27 3-(4-substituted)halodiazirines, the need is stressed to handle the compounds at below 30°C to prevent thermal decomposition, or, for the pure compounds, explosion [3].

Individually indexed compounds are:
3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2645
3-Chloro-3-methoxydiazirine, 0734
Chloro-(4-methoxyphenyl)diazirine, 2928
3-Chloro-3-methyldiazirine, 0733
3-Chloro-3-trichloromethyldiazirine, 0610
3-Chloro-3-trifluoromethyldiazirine, 0593
Diazirine, 0405
Diazirine-3,3-dicarboxylic acid, 1080
Difluorodiazirine, 0342
Dipotassium diazirine-3,3-dicarboxylate, 1340
3-Fluoro-3-(trifluoromethyl)-3*H*-diazirine, 0631
3-Methyldiazirine, 0808
3,3-Pentamethylenediazirine, 2422
Potassium hydrogen diazirine-3,3-dicarboxylate
3-Propyldiazirine, 1594
Spiro(homocubane-9,9′−diazirine)(Spiro[3*H*-diazirine-3,9−pentacyclo [4,3,0,$0^{2,5}0^{3,8}0^{4,7}$]nonane]), 3127
See related AZO COMPOUNDS

DIAZOAZOLES

1. Hui, H. *et al., Tetrahedron Lett.*, 1982, **23**, 5115−5118
2. Magee, W. L. *et al, J. Org. Chem.*, 1987, **52**, 5538−5548
Four 4-diazo-1,2,3-triazole derivatives, though stable in dichloromethane solution, exploded violently when heated as solids [1]. Several diazo-triazoles, -pyrazoles and -imidazoles were found to be explosively unstable in varying degrees [2].

Individually indexed compounds are :
5-Amino-3-phenyl-1,2,4-triazole, : Nitrous acid
5-*tert*-Butyl-3-diazo-3*H*-pyrazole
5-Cyano-4-diazo-4*H*-1,2,3-triazole
2-Diazo-2H-imidazole
3-Diazo-5-phenyl-3*H*-pyrazole
3-Diazo-5-phenyl-3*H*-1,2,4-triazole
4-Diazo-1,2,3-triazole
3-Diazo-3*H*-1,2,4-triazole
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate

DIAZO COMPOUNDS CN_2

In this group of reactive and unstable compounds, the common structural feature is an N=N unit double-bonded to a carbon atom. Individually indexed compounds are:

1-Benzoyl-1-phenyldiazomethane, 3638
1,6-Bis(4-chlorophenyl)-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3743
∗ Bis(dimethylarsinyldiazomethyl)mercury, 2467
Bis(ethoxycarbonyldiazomethyl)mercury, 2978
2-Buten-1-yl diazoacetate, 2377
tert-Butyl diazoacetate, 2423
tert-Butyl 2-diazoacetoacetate, 3009
5-*tert*-Butyl-3-diazo-3*H*-pyrazole, 2831
Cyanodiazoacetyl azide, 1346
5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1345
Diazoacetaldehyde, 0710
Diazoacetonitrile, 0675
Diazoacetyl azide, 0679
2-Diazocyclohexanone, 2375
Diazocyclopentadiene, 1832
2-Diazo-2H-imidazole, 1082
1-Diazoindene, 3116
Diazomalonic acid, 1081
Diazomalononitrile, 1344
Diazomethane, 0406
5-(Diazomethylazo)tetrazole, 0719
Diazomethyldimethylarsine, 1240
3-Diazo-5-phenyl-3*H*-pyrazole, 3118
4-Diazo-5-phenyl-1,2,3-triazole, 2910
3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2909
3-Diazopropene, 1135
α-Diazo-γ-thiobutyrolactone, 1434
4-Diazo-1,2,3-triazole, 0678
3-Diazo-3*H*-1,2,4-triazole, 0677
Di-*tert*-butyl diazomalonate, 3411
Dicyclopropyldiazomethane, 2824
Dideuterodiazomethane, 0336
Diethyl diazomalonate, 2828
Dinitrodiazomethane, 0545
1,6-Diphenyl-2,5-bis(diazo)-1,3,4,6-tetraoxohexane, 3744
Disilver diazomethanide, 0306
Ethyl diazoacetate, 1503
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1853
Lithium diazomethanide, 0379
3-Methoxy-2-nitrobenzoyldiazomethane, 3124
Methyl diazoacetate, 1138
2-Nitrophenylsulfonyldiazomethane, 2700

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Phenyldiazomethane, 2725
Poly(diazomethylenemercury), 0522
Sodium diazomethanide, 0383
Tetrachlorodiazocyclopentadiene, 1807
2,2,2-Trifluorodiazoethane, 0664

See α-DIAZO-β-OXOSULFONES, DIAZOMETHANE SALTS

DIAZOMETHANE SALTS **$Met_2C{=}N{=}N$**

Bertrand, G. *et al., Angew. Chem. (Int.),* 1994, **33**(5), 534.

The disilver, dilithium and 'dimercury' salts of this anion [128234-64-0] are too explosive for safe handling. The bis(trimethylstannyl) derivative is a safer substitute.

See DIAZO COMPOUNDS

DIAZONIUM CARBOXYLATES **$N_2^+ArCO_2^-$**

Several of these internal diazonium salts, prepared by diazotisation of anthranilic acids, are explosive in the solid state, or react violently with various materials. Individually indexed compounds (including analogous sulfonates) are:

Benzenediazonium-2-carboxylate, 2659
Benzenediazonium-3 or 4-carboxylate, 2661
∗ Benzenediazonium-2-sulfonate, 2192
∗ Benzenediazonium-4-sulfonate, 2193
∗ 2-Carboxy-3,6-dimethylbenzenediazonium chloride, 3138
∗ 1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3392
3,5-Dimethylbenzenediazonium-2-carboxylate, 3128
4,6-Dimethylbenzenediazonium-2-carboxylate, 3129
4-Hydroxybenzenediazonium-3-carboxylate, 2663
∗ 2-Hydroxy-6-nitro-1-naphthalenediazonium-4-sulfonate, 3240
4-Iodobenzenediazonium-2-carboxylate, 2639

See other DIAZONIUM SALTS

DIAZONIUM PERCHLORATES **$ArN_2^+\ ClO_4^-$**

1. Hofmann, K. A. *et al., Ber.,* 1906, **39**, 3146; 1910, **43**, 2624
2. Vorländer, D., *Ber.,* 1906, **39**, 2713–2715
3. Burton, H. *et al., Analyst,* 1955, **80**, 4

The diazonium perchlorates are extremely explosive, shock-sensitive materials when dry, some even when damp [1,2]. The salt derived from diazotised *p*-phenylendiamine was considered to be more explosive than any other substance known in 1910 [3]. Individually indexed compounds are:

4-Aminobenzenediazonium perchlorate, 2304
Benzene-1,4-bis(diazonium perchlorate), 2160
Benzenediazonium perchlorate, 2232
4,4′-Biphenylenebis(diazonium) perchlorate, 3457

1(2′-Diazoniophenyl)2-methyl-4,6-diphenylpyridinium diperchlorate, 3847
1(2′-, 3′-, or 4′-Diazoniophenyl)-2,4,6-triphenylpyridinium diperchlorate, 3870
1- or 2-Naphthalenediazonium perchlorate, 3247
3-Nitrobenzenediazonium perchlorate, 2155
2-Toluenediazonium perchlorate, 2740
See other DIAZONIUM SALTS

DIAZONIUM SALTS ArN_2^+

1. Houben-Weyl, 1965, Vol. 10.3, 32–38
2. Doyle, W. H., *Loss Prev.*, 1969, **3**, 14
3. Anon., *Sichere Chemiearbeit*, 1993, **45**(1), 8
4. Fogel'zang, A. E. *et al.*, *Chem. Abs.*, 1974, **81**, 155338
5. Bartsch, R. A. *et al.*, *J. Amer. Chem. Soc.*, 1976, **98**, 6753–6754
6. Storey, P. D., *Runaway Reactions*, 1981, Paper 3/P, 1–9
7. Mustacchi, H. *et al.*, Ger. Offen. DE 3 202 208, 1982
8. Grewer, Th. *et al.*, *Thermochim. Acta*, 1993, **225**(2), 201

A few diazonium salts are unstable in solution, and many are in the solid state. Of these, the azides, chromates, nitrates, perchlorates (outstandingly), picrates, sulfides, triiodides and xanthates are noted as being explosive, and sensitive to friction, shock, heat and radiation. In view of their technical importance, diazonium salts are often isolated as their zinc chloride (or other) double salts, and although these are considerably more stable, some incidents involving explosive decomposition have been recorded.

During bottom discharge of an undefined diazonium chloride preparation, operation of a valve initiated explosion of the friction-sensitive chloride which had separated from solution. The latter did not occur with the corresponding sulfate [2]. Some of a group of industrial diazotisation vessels were closed down, improving gas extraction from those still operated. The ventline later blocked on one vessel and, when attempts were made to open it, disassembled itself explosively. Thick deposits of crystalline diazonium salts were found elsewhere in the system, although only slime had been seen previously. It appears that the improved extraction sucked amines and nitrous gases from the vessels, to complete their reaction in the vent line [3]. The combustive and explosive behaviour of solid diazonium salts at various pressures was studied, including benzenediazonium chloride and nitrate, and *m*- and *p*-nitrobenzenediazonium chlorides [4]. Complexation of diazonium anions with crown ethers reduces or suppresses thermal decomposition of the anion, and may prove useful to stabilise shock-sensitive species [5]. The thermal explosion properties of a series of 10 dimethylamino- or morpholino-substituted benzenediazonium tetrafluoroborates or tetrafluorozincates were studied using DSC, to provide data to assist in practical assessment of stability, particularly towards impact [6]. Diazonium 5-sulfoisophthalate salts are more thermally stable and less flammable than the corresponding tetrafluoroborate and tetrachlorozincate salts [7]. A procedure is given for testing impact sensitivity of diazonium salts by a drop-weight procedure. It is applicable to impure materials of commercial practice. Nitrobenzenediazonium

DropBooks

derivatives were found especially sensitive: of critical impact energy 1–2 J [8]. Separately treated groups are:

ARENEDIAZONIUM OXIDES, DIAZONIUM CARBOXYLATES
DIAZONIUM PERCHLORATES, DIAZONIUM SULFATES
DIAZONIUM SULFIDES AND DERIVATIVES
DIAZONIUM TETRAHALOBORATES, DIAZONIUM TRIIODIDES

Individually indexed compounds are:

5-Amino-3-phenyl-1,2,4-triazole, : Nitrous acid, 2952
Benzenediazonium chloride, 2230
Benzenediazonium iodide, 2250
Benzenediazonium nitrate, 2275
∗ Benzenediazonium-2-sulfonate, 2192
∗ Benzenediazonium-4-sulfonate, 2193
Benzenediazonium tetrachlorozincate, 3476
Benzenediazonium tribromide, 2227
∗ 1,10-Bis(diazonio)decaboran(8)ate, 0197
4-Bromobenzenediazonium salts, 2131
2-Chlorobenzenediazonium salts, 2148
3-Chlorobenzenediazonium salts, 2149
4-Chloro-2-methylbenzenediazonium salts, 2719
5-Chlorotoluene-2-diazonium tetrachlorozincate, 3644
2-Diazonio-4,5-dicyanoimidazolide, 2050
1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3392
3-Diazoniopyrazolide-4-carboxamide, 1399
5-Diazoniotetrazolide, 0548
2-Naphthalenediazonium trichloromercurate, 3248
4-Nitrobenzenediazonium azide, 2209
3-Nitrobenzenediazonium chloride, 2151
4-Nitrobenzenediazonium nitrate, 2205
∗ Potassium 1-phenylethanediazoate, 2964
Tetrazole-5-diazonium chloride, 0370
2-Toluenediazonium bromide, 2736
2- or 3-Toluenediazonium iodide, 2751
3-Toluenediazonium salts, 2774
2- or 4-Toluenediazonium salts, 2775
2,4,6-Tri(2-acetylhydrazino)-1,3,5-trinitrobenzene, : Hydrochloric acid, 3535
1,2,4-Triazole-3-diazonium nitrate, 0680
3,4,5-Triiodobenzenediazonium nitrate, 2084

See also TETRAZOLES

DIAZONIUM SULFATES $(ArN_2^+)_2\ SO_4^{2-}$, $ArN_2^+\ HSO_4^-$

Bersier, P. *et al., Chem. Ing. Tech.*, 1971, **43**(24), 1311–1315

During investigation after the violent explosion of a 6-chloro-2,4-dinitrobenzenediazonium sulfate preparation made in nitrosylsulfuric acid, it was found that above

certain minimum concentrations some diazonium sulfates prepared in sulfuric acid media could be brought to explosive decomposition by local application of thermal shock. Classed as dangerous were the diazonium derivatives of 6-chloro-2,4-dinitroaniline (at 1.26 mmol/g, very dangerous at 1.98 mmol/g); 6-bromo-2,4-dinitroaniline (very dangerous at 1.76 mmol/g); 2,4-dinitroaniline (2.0 mmol/g). Classed as suspect were the diazonium derivatives above at lower concentrations, and those of 2-chloro-5-trifluoromethylaniline (at 1.84 mmol/g); 2,6-dichloro-4-nitroaniline (0.80 mmol/g); 2-methanesulfonyl-4-nitroaniline (0.80 mmol/g); 2-cyano-4-nitroaniline (1.04 mmol/g). A further 11 derivatives were not found to be unstable. Details of several stability testing methods are given. Individually indexed compounds are:

Benzenediazonium hydrogen sulfate, 2318
6-Bromo-2,4-dinitrobenzenediazonium hydrogen sulfate, 2097
2-Chloro-4,6-dinitroaniline, : Nitrosylsulfuric acid, 2153
6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2102
2-Chloro-5-trifluoromethylbenzenediazonium hydrogen sulfate, 2647
2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2668
2,6-Dichloro-4-nitrobenzenediazonium hydrogen sulfate, 2106
2,4-Dinitrobenzenediazonium hydrogen sulfate, 2206
2-Methanesulfonyl-4-nitrobenzenediazonium hydrogen sulfate, 2784

See THERMAL STABILITY OF REACTION MIXTURES
See other DIAZONIUM SALTS

DIAZONIUM SULFIDES AND DERIVATIVES ArN_2S-

DropBooks

1. Graebe, C. *et al.*, *Ber.*, 1882, **15**, 1683
2. Bamberger, E. *et al.*, *Ber.*, 1896, **29**, 272
3. Nawiasky, P. *et al.*, *Chem. Eng. News*, 1945, **23**, 1247
4. Hodgson, H. H., *Chem. & Ind.*, 1945, 362
5. Tomlinson, W. R., *Chem. Eng. News*, 1957, **29**, 5473
6. Hollingshead, R. G. W. *et al.*, *Chem. & Ind.*, 1953, 1179
7. Anon., *Angew. Chem. (Nachr.)*, 1962, **10**, 278
8. Parham, W. E. *et al.*, *Org. Synth.*, 1967, **47**, 107
9. Anon., *BCISC Quart. Safety Summ.*, 1969, **40**, 17
10. Zemlyanskii, N. I. *et al.*, *Chem. Abs.*, 1971, **74**, 53204
11. Spencer, H., *Chem. Brit.*, 1977, **13**, 240–241
12. Petullo, G. *et al.*, *Tetrahedron Lett.*, 1985, **24**, 6365–6368

There is a long history of the preparation of explosive solids or oils from interaction of diazonium salts with solutions of various sulfides and related derivatives. Such products have arisen from benzene- and toluene-diazonium salts with hydrogen, ammonium, or sodium sulfides [1,5]; 2- or 3-chlorobenzene-, 4-chloro-2-methylbenzene-, 2- or 4-nitrobenzene- or 1- or 2-naphthalene-diazonium solutions with hydrogen sulfide, sodium hydrogen sulfide or sodium mono-, di- or poly-sulfides [1]–[4,7]. 4-Bromobenzenediazonium solutions gave with hydrogen sulfide at −5°C a product which exploded under water at 0°C [2], and every addition of a drop of 3-chlorobenzenediazonium solution to sodium disulfide solution

at 0°Caused a violent explosion [4]. In general, these compounds appear to be bis(arenediazo) sulfides or the hydrogen sulfides, since some of the corresponding disulfides are considerably more stable [2].

Interaction of 2-, 3- or 4-chlorobenzenediazonium salts with *O*-alkyldithiocarbonate ('xanthate') solutions [8] or thiophenoxide solutions [9] produces explosive products, possibly arenediazo aryl sulfides. The intermediate diazonium xanthate produced during the preparation of *m*-thiocresol can be dangerously explosive under the wrong conditions [8], while the reaction of 3-nitrobenzenediazonium chloride with xanthate solution at 70−75°C proceeds with near-explosive evolution of nitrogen [4]. The product of interaction of 2-chlorobenzenediazonium chloride and sodium 2-chlorothiophenoxide exploded violently on heating to 100°C, and the oil precipitated from interaction of potassium thiophenoxide with 3-chlorobenzenediazonium chloride exploded during mixing of the solutions [9].

Interaction of substituted arenediazonium salts with potassium *O,O*-diphenylphosphorodithioates gave a series of solid diazonium salts which decomposed explosively when heated dry [10]. The unique failure of diazotised anthranilic acid solutions to produce any explosive sulfide derivatives under a variety of conditions has been investigated and discussed [6]. Preparation of diaryl sulfides from interaction of diazonium and thiophenoxide salts led to violent explosions, attributed to presence of some arenediazo sulfide during subsequent distillation of the diaryl sulfides. Precautions are detailed [11]. A safe method of preparation of diaryl sulfides from diazonium tetrafluoroborates and sodium benzenethiolate in DMF is now available [12].

Individually indexed hazardous reaction pairs are:
4-Chloro-2-methylbenzenediazonium salts, 2719
Hydrogen trisulfide : Benzenediazonium chloride, 4485
1-Naphthalenediazonium salts, 3251
2-Naphthalenediazonium salts, 3252
2- or 4-Toluenediazonium salts, 2775
3-Toluenediazonium salts, : Ammonium sulfide, or Hydrogen sulfide, 2774
3-Toluenediazonium salts, : Potassium *O*-ethyl dithiocarbonate
See Hydrogen trisulfide: Benzenediazonium chloride

DIAZONIUM TETRAHALOBORATES $ArN_2^+ BX_4^-$

1. Olah., G. A. *et al., J. Org. Chem.*, 1961, **26**, 2053
2. Doak, G. O. *et al., Chem. Eng. News*, 1967, **45**(53), 8
3. Fletcher, T. L., *Chem. & Ind.*, 1972, 370
4. Pavlath, A. E. *et al., Aromatic Fluorine Compounds*, 15, New York, Reinhold, 1962
5. Coates, C. F. *et al., Runaway Reactions*, 1981, Paper 4/Y, 1−2

Solid diazonium tetrachloroborates decompose very vigorously, sometimes explosively, on heating in absence of solvent. Dry *o*-nitrobenzenediazonium tetrachloroborate is liable to explode spontaneously during storage at ambient temperature [1]. Hazards involved in drying diazonium tetrafluoroborates have been discussed. The

decomposition temperature of any new salt should be checked first on a small sample, and only if it is above 100°C should the bulk be dried and stored. Salts which show signs of decomposition at or below ambient temperature must be kept moist and used immediately [2]. The need to use an inert solvent in any deliberate thermal decomposition is stressed [3], and attention is drawn to an erroneous reference to the use of tetrahydrofuran, which could be hazardous. The presence of nitro substituent groups may greatly increase the decomposition temperature, so that decomposition may become violent or even explosive [4]. The Schiemann thermal decomposition of a tetrafluoroborate salt, previously done repeatedly without incident, became violent on one occasion, causing vessel pressurisation from evolved gas. The presence of impurities had transformed the normally smooth decomposition at 95° to a violent reaction at 84°C [5].

Individually indexed compounds are:
2-Azidomethylbenzenediazonium tetrafluoroborate, 2708
Benzenediazonium tetrafluoroborate, 2223
2-Chloro-3-pyridinediazonium tetrafluoroborate, 1816
5-(4-Diazoniobenzenesulfonamido)thiazole tetrafluoroborate, 3119
5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3677
2-Nitrobenzenediazonium tetrachloroborate, 2128
3-Pyridinediazonium tetrafluoroborate, 1826
See other GAS EVOLUTION INCIDENTS, CATALYTIC IMPURITY INCIDENTS

DIAZONIUM TRIIODIDES $ArN_2^+ I_3^-$

DropBooks

Carey, J. G. *et al., Chem. & Ind.*, 1960, 7
The products produced by interaction of diazonium salts and iodides are unstable and liable to be explosive in the solid state. They are usually the triiodides, but monoiodides have been isolated under specific conditions from diazotised aniline and *o*-toluidine. Products prepared from diazotised *o*-, *m*- or *p*-nitroanilines, *m*-chloro-, -methoxy-, or -methyl-aniline are too unstable to isolate, decomposing below 0°C.

Individually indexed compounds are:
Benzenediazonium iodide, 2250
Benzenediazonium triiodide, 2254
4-Chlorobenzenediazonium triiodide, 2137
2,4-Dimethylbenzenediazonium triiodide, 2963
2- or 4-Methoxybenzenediazonium triiodide, 2758
4-Toluenediazonium triiodide, 2756
See other DIAZONIUM SALTS, IODINE COMPOUNDS

α-DIAZO-β-OXOSULFONES $RSO_2CN_2CO.R'$

Manteiro, H. J., *Synth. Comm.*, 1987, **17**(8), 983–989

The title compounds were prepared safely by a diazo-transfer reaction onto β-oxosulfones by treatment with 1-ethyl-2-chloropyridinium tetrafluoroborate and sodium azide in presence of sodium acetate.

See DIAZO COMPOUNDS, above

DIAZOTISATION $\mathbf{ArNH_2 \rightarrow ArN_2^+}$

1. Houben-Weyl, 1965, Vol. 10.3, 1–112
2. Schierwater, F.-W., *Sichere Chemiearb.*, 1986, **38**(2), 18

In the extensive review of diazotisation, frequent reference is made to the need for close temperature control during processing operations, and to the explosive nature of isolated diazonium salts [1]. Inclusion of methanol in the reaction mixture used to diazotise 2-toluidine, and use of sulfuric acid rather than acetic acid in the ensuing coupling reaction with 2-toluidine to give 2-aminoazotoluene led to formation of a high concentration of methyl nitrite. No explosion occurred, but a fatality resulted from inhaling the fumes escaping from the open port of the reaction vessel [2].

See also Many examples are covered in the group entries:
ARENEDIAZONIUM OXIDES, DIAZONIUM CARBOXYLATES
DIAZONIUM PERCHLORATES, DIAZONIUM SULFATES
DIAZONIUM SULFIDES AND DERIVATIVES
DIAZONIUM TETRAHALOBORATES, DIAZONIUM TRIIODIDES

See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

See other DIAZO COMPOUNDS, HIGH-NITROGEN COMPOUNDS, TRIAZOLES

***I,I*-DI(BENZOYLPEROXY)ARYLIODINES** $\mathbf{(XC_6H_4CO.OO)_2IC_6HY}$

Plesnicar, B. *et al.*, *Angew Chem. (Intern. Ed.)*, 1970, **9**, 707

Compounds of the general structure above, with X = *m*-chloro or *p*-nitro, and Y = H, *p*-chloro or *o*-methoxy, are extremely powerful oxidants, unstable when dry, and will explode during manipulation at ambient temperature (particularly with metal spatulae), or on heating to 80–120°C. The group exceeds the oxidising power of organic peroxyacids. The individual compounds are:

I,I-Bis(3-chlorobenzoylperoxy)-4-chlorophenyliodine, 3793
I,I-Bis(3-chlorobenzoylperoxy)phenyliodine, 3794
I,I-Bis(4-nitrobenzoylperoxy)-4-chlorophenyliodine, 3789
I,I-Bis(4-nitrobenzoylperoxy)-2-methoxyphenyliodine, 3819
I,I-Bis(4-nitrobenzoylperoxy)phenyliodine, 3795
[*I,I*Bis(trifluoroacetoxy)iodo]benzene, 3239

See other DIACYL PEROXIDES, IODINE COMPOUNDS, OXIDANTS

DICHROMATE SALTS OF NITROGENOUS BASES $\mathbf{(N^+)_2Cr_2O_7^{2-}}$

Gibson, G. M., *Chem. & Ind.*, 1966, 553

The dichromates of 1-phenylbiguanide, its *p*-chloro, *p*-methyl and 1-naphthyl analogues all decompose violently at around 130°C.

Individually indexed compounds are:
Ammonium dichromate, 4246
1-(4-Chlorophenyl)biguanidinium hydrogen dichromate, 3005
Dianilinium dichromate, 3537
Dipyridinium dichromate, 3304
Guanidinium dichromate, 0971
1-Phenylbiguanidinium hydrogen dichromate, 3019
4-Tolylbiguanidium hydrogen dichromate, 3182
See other OXOSALTS OF NITROGENOUS BASES

[14] DIENE-N_4 COMPLEXES

1. Goedken, V. L. *et al., J. Amer. Chem. Soc.*, 1972, **94**, 3397
2. Tait, A. M. *et al., Inorg. Synth.*, 1978, **18**, 2–36
3. Peng, S. M. *et al., Inorg. Chem.*, 1978, **17**, 821

The macroheterocylic ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene (abbreviated to [14] diene-N_4) forms cationic complexes with iron(II or III), also containing acetonitrile, imidazole, phenanthroline or halogen ligands. When the anion is perchlorate, the products are explosive, sensitive to heat and impact; some appear to decompose on storage (1 week) and become sensitive to slight disturbance [1]. Details are given for avoiding the use of perchloric acid and/or perchlorate salts in this and structurally related series [2]. Some of the compounds containing perchlorate anions must be regarded as extremely hazardous and potentially explosive. Prepare only minimal amounts, and long term storage above 1 month is not recommended [3]. Individually indexed compounds are:

Acetonitrileimidazole-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3828
∗ *trans*-Bromoazido(meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) perchlorate, 3553
Bromo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclo-tetradecadieneiron(II) perchlorate, 3722
Chloro-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3724
Copper(II) perchlorate: Polyfunctional amines, 4057
Copper(II) perchlorate: *N*-(2-Pyridyl)acylacetamides, 4057
Diacetonitrile-5,5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3813
Dichloro-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(III) perchlorate, 3725
5,5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraaza-4,11,-cyclotetradecadiene-1,10-phenanthrolineiron(II) perchlorate, 3869
Hydroxobis[5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II)] triperchlorate, 3881
Iodo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II) perchlorate, 3723

BioBooks

Oxybis[aqua-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadieneiron(II)] tetraperchlorate, 3882

See POLYAZACAGED METAL PERCHLORATES

See other AMMINEMETAL OXOSALTS

DIENES **C=C=C, C=C−C=C**

The 1,2 and 1,3-dienes (vicinal and conjugated, respectively) are more reactive than the separated dienes.

Oxides of nitrogen

See Nitrogen oxide: Dienes, Oxygen

Individually indexed compounds are:

7-Azidobicyclo[2.2.1]hepta-2,5-diene, 2777
∗ 1,4-Benzoquinone diimine, 2310
∗ 1,4-Benzoquinone monoimine, 2260
† Bicyclo[2.2.1]hepta-2,5-diene, 2789
† 1,2-Butadiene, 1479
† 1,3-Butadiene, 1480
† 2-Chloro-1,3-butadiene, 1451
∗ *N*-Chlorocinnamaldimine, 3126
† 1,3,5-Cycloheptatriene, 2790
† 1,3-Cyclohexadiene, 2361
† 1,4-Cyclohexadiene, 2362
† 1,3,5,7-Cyclooctatetraene, 2943
∗ 1,3,5-Cyclooctatriene, 2966
† Cyclopentadiene, 1857
2,3-Diazido-1,3-butadiene, 1437
† Dicyclopentadiene, 3299
2,3-Dimethyl-1,3-butadiene, 2407
∗ 3,7-Dimethyl-2,6-octadienal, 3346
† 1,3-Hexadiene, 2409
† 1,4-Hexadiene, 2410
† 1,5-Hexadiene, 2411
† *cis*-2-*trans*-4-Hexadiene
† *trans*-2-*trans*-4-Hexadiene, 2412
1,3-Hexadien-5-yne, 2290
† 1,5-Hexadien-3-yne, 2291
4,5-Hexadien-2-yn-1-ol, 2328
1-Iodohexa-2,4-diene, 2393
Limonene, 3337
1,5-*p*-Menthadiene, 3338
∗ Methoxy-1,3,5,7-cyclooctatetraene, 3149
† 2-Methyl-1,3-butadiene, 1893
† 3-Methyl-1,2-butadiene, 1892

Methylcyclopentadiene, 2363
† 2-Methyl-1,3-pentadiene, 2416
† 4-Methyl-1,3-pentadiene, 2417
∗ 2-Nitrosophenol (1,2-Benzoquinone monoxime), 2263
† 1,7-Octadiene, 3021
∗ 1,3,7-Octatrien-5-yne, 2944
† 1,2-Pentadiene, 1895
† 1,3-Pentadiene, 1896
† 1,4-Pentadiene, 1897
Perfluorobutadiene, 1364
∗ Poly(acetylene), 0687
∗ *cis*-Poly(butadiene), 1484
∗ Poly(1-pentafluorothio-1,2-butadiyne), 1379
† Propadiene (Allene), 1124
1,1,2,3-Tetrachloro-1,3-butadiene, 1389
∗ 1,1,4,4-Tetrachlorobutatriene, 1360
Tetracyclo[4.3.0^{3,5}.0^{4,6}]nona-1,7-diene, 3125
∗ 1,1,4,4-Tetrafluorobutatriene, 1363
See other PEROXIDISABLE COMPOUNDS

DIESEL ENGINES

1. Sheldrick, G., *Chem. & Ind.*, 1969, 1823
2. Young, J. A., *CHAS Notes*, 1991, **IX**(5), 2
3. Bond, 1991, 50

In the vicinity of hydrocarbon or solvent spillages, these engines may take in enough fuel with their air supply. In consequence, they cannot be stopped by cutting the supply of fuel from the tank, perpetuating combustion which may not stay internal [1,3]. Precautions against flashback are detailed. Problems can also arise if the engine is driving the pump which is spilling the volatile material [2]. Similar problems could, in principle, occur with gas turbines.

DropBooks

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

1. Gygax, R. *et al., Therm. Anal.*, 1980, **1**, 541–548
2. Brogli, F. *et al., Therm. Anal.*, 1980, **1**, 549–554
3. Cardillo, P. *et al., Runaway Reactions*, 1981, Paper 3/N, 1–9

The scope and limitations of the use of DSC as a means of investigating the reaction dynamics of potentially hazardous chemical reactions is discussed. For existing processes, examination of production samples taken at various stages of the overall process sequence can identify the stage at which maximum heat production is occurring, as the most critical phase for control requirements. The existence of an induction period can also be established, and use of the instrument in its more sensitive isothermal mode can yield information on consecutive reactions and catalytic effects [1]. The place of DSC in a screening programme to estimate hazards in proposed chemical processes is discussed in detail. The use of pressure-tight encapsulated samples permits rapid assessment of heats of reaction and/or

decomposition and kinetic behaviour under likely process conditions. Selected case studies are included [2]. The part played by DSC in the investigation of the Seveso incident has been discussed [3].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

DIFFERENTIAL THERMAL ANALYSIS (DTA)

1. Corignan, Y. P. *et al., J. Org. Chem.*, 1967, **32**, 285
2. Prugh, R. W., *Chem. Eng. Progr.*, 1967, **63**(11), 53
3. Krien, G., *Diff. Therm. Anal.*, 1972, **2**, 353–377
4. Duswalt, A. A., *Thermochim. Acta*, 1974, **8**(1–2), 57–58
5. Berthold, W. *et al., Chem. Ing. Tech.*, 1975, **47**, 368–373
6. Giger, G. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, C14–23, Rugby, IChE, 1983
7. Cassel, R. B., *Perkin-Elmer Therm. Anal. Appl. Study*, 1979, **28**, 1–6

Thermal stabilities of 40 explosive or potentially explosive *N*-nitroamines, aminium nitrates and guanidine derivatives were studied in relation to structure; 14 of the compounds decomposed violently when the exotherm occurred [1]. The value of the DTA technique in assessing hazards of compounds or reaction mixtures is discussed [2]. DTA data on thermally unstable materials (peroxides) as well as explosives was reviewed [3]. The use of various DTA methods for defining processing, storage, and safe reaction conditions has been investigated, and experiences and conclusions were discussed [4]. Use of DTA and DSC methods for predictions in preventing thermal explosions by assessing the stable range of operations in large storage containers are discussed [5,6], with experimental details and exemplification using nonyl nitrate [5] and an unidentified compound [6]. Details of a new ASTM standard method E537-76 for determination of potential explosive hazard by studying the kinetics of thermal decomposition by DTA were discussed [7].

Some of the individual compounds examined are :
Ammonium 1,2-ethylenebis(nitramide)
3-Azoniabicyclo[3.2.2]nonane nitrate
N,N′-Diacetyl-*N,N′*-dinitro-1,2-diaminoethane
Diaminoguanidinium nitrate
1,3-Dinitro-2-imidazolidinone
N,N′-Dinitro-*N*-methyl-1,2-diaminoethane
1,3,6,8-Tetraazoniatricyclo[6.2.1.$1^{3,6}$]dodecane tetranitrate
1,3,5,7-Tetranitroperhydro-1,3,5,7-tetrazocine
Triaminoguanidinium nitrate
Triaminoguanidinium perchlorate

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

DIFLUOROAMINOALKANOLS $F_2NC(RR')OH$

Fokin, A. V. *et al., Chem. Abs.*, 1970, **72**, 78340

A series of 1-difluoroaminoalkanols prepared from difluoramine and an aldehyde or ketone, together with their acetates or bis(ethers), were all shock- and friction-sensitive explosives.

See other DIFLUOROAMINO COMPOUNDS

DIFLUOROAMINO COMPOUNDS RNF_2

Freeman, J. P., *Adv. Fluorine Chem.*, 1970, **6**, 321, 323

All organic compounds containing one or more difluoroamino groups should be treated as explosive oxidants and excluded from contact with strong reducing agents. If the ratio of NF_2 to CH_2 groups is above 1:5, the compound will be impact-sensitive. Direct combustion for elemental analysis will be unsafe, but polarography is applicable. Some difluoroamines have been studied as explosives in their own right.

Individually indexed compounds are:

Bis(difluoroamino)difluoromethane, 0362
1,1-Bis(difluoroamino)-2,2-difluoro-2-nitroethyl methyl ether, 1104
1,2-Bis(difluoroamino)ethanol, 0802
1,2-Bis(difluoroamino)ethyl vinyl ether, 1496
4,4-Bis(difluoroamino)-3-fluoroimino-1-pentene, 1867
1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0803
2-Cyano-1,2,3-tris(difluoroamino)propane, 1432
Di-1,2-bis(difluoroaminoethyl) ether, 1497
(Difluoroamino)difluoroacetonitrile, 0630
3-Difluoroamino-1,2,3-trifluorodiaziridine, 0358
N,N-Difluorotrifluoromethylamine, 0357
1,1-Difluorourea, 0398
∗ Pentafluoroguanidine, 0359
C,N-Perfluoro-*N*-aminomethyltriaminomethane, 0649
Perfluoro-*N*-cyanodiaminomethane, 0637
† Tetrafluorohydrazine, 4345
Tetrafluorourea, 0352
Tris(difluoroamino)fluoromethane, 0364

See BIS(DIFLUOROAMINO)ALKYL NITRATES *See other* N-HALOGEN COMPOUNDS

DIFLUOROAMINOPOLYNITROARYL COMPOUNDS

Lerom, M. W. *et al., J. Chem. Eng. Data*, 1974, **19**, 389–392

Several difluoroaminopolynitro derivatives of stilbene, biphenyl, terphenyl and their precursors are explosives, sensitive to initiation by impact, shock, friction or rapid heating.

See other DIFLUOROAMINO COMPOUNDS

DropBooks

DIFLUOROPERCHLORYL SALTS $F_2ClO_2^+ Z^-$

Organic materials, or Water

Christe, K. O. *et al., Inorg. Chem.*, 1973, **12**, 1358

Difluoroperchloryl tetrafluoroborate, hexafluoroarsenate or hexafluoroplatinate all react violently with organic materials or water. Individual salts are:

Difluoroperchloryl hexafluoroarsenate, 0093

Difluoroperchloryl hexafluoroplatinate, 3991

Difluoroperchloryl tetrafluoroborate, 0123

See Chlorine dioxygen trifluoride

DIGESTION

Geological and biological sample preparation for subsequent analysis often involves digestion in highly oxidant media such as nitric or perchloric acid. This is a frequent cause of incidents, which will be found under the entries for digestion reagents. It is also necessary to consider that the apparatus, or parts of it such as mounts and sealing rings, may be constructed of materials themselves digestible.

DIISOCYANIDE LIGANDS $:C{=}N{-}C[CH_2]_nC{-}N{=}C:$

1. Yaneff, P. V. *et al., J. Organomet. Chem.*, 1979, **179**, 111
2. Howell, J. A. *et al., J. Chem. Soc., Dalton Trans.*, 1981, 301

It is preferable to prepare and use various diisocyanide ligands (trimethylene to octamethylenene diisocyanides, 1,4-dimethylenecyclohexane and 1,3-xylylidene diisocyanides) as solvent solutions rather than as isolated materials, because violent explosions have been observed during vacuum distillation of these ligands [1]. Four such ligands were, however, distilled uneventfully [2]. Individually indexed compounds are:

1,3-Bis(isocyanomethyl)benzene, 3257

1,4-Bis(isocyanomethyl)cyclohexane, 3330

1,4-Diisocyanobutane, 2372

1,6-Diisocyanohexane, 3006

1,8-Diisocyanooctane, 3343

1,5-Diisocyanopentane, 2825

1,3-Diisocyanopropane, 1869

1,1,1-Triazidodinitroethane, 0683

See related CYANO COMPOUNDS

1,1-DINITRODIFLUORAMINES $RC(NO_2)_2NF_2$

Fokin, A. V. *et al., Dokl, Akad. Nauk.*, 1996, **346**(3), 358; *Chem. Abs.*, 1996, **125** 167297

A variety of these compounds were prepared (R = CN, $CONH_2$, Me, Ph). Not surprisingly they were explosives very sensitive to shock, friction and heat. They were inclined to distillation during distillation.

See also *N*-HALOGEN COMPOUNDS, POLYNITROALKYL COMPOUNDS

Preparative hazard
See Sodium chlorate: Alkenes, Potassium osmate

1,3,4-DIOXAZOLONES

Middleton, W. J., *J. Org. Chem.*, 1983, **48**, 3845−3847
2-Perfluoroalkyl-1,3,4-dioxazolones are a potentially hazardous group of compounds, being capriciously explosive. They are no safer than perfluoroacyl azides as precursors for isothiocyanates.
See other N−O COMPOUNDS, DIOXETANES

DIOXETANES

1. Mumford, C., *Chem. Brit.*, 1975, **11**, 402
2. Kopecky, K. R. *et al., Can. J. Chem.*, 1975, **53**, 1103−1122
3. Livingstone, R., Rodd, (Supplement to 2nd Edn.), IVa, 1984
4. Adam, W. *et al., J. Amer. Chem. Soc.*, 1994, **116**(17), 7581

This group of highly strained cyclic peroxides, though thermodynamically unstable, contains some compounds of sufficient kinetic stability to exist as solids at ambient temperature [1]. Interest in these compounds is increasing, most are very unstable, several have proved explosive when isolated [2,3]. Not only are lower 1,2-dioxetanes dangerously unstable but so, above 0°C, are the precursor 1,2-bromohydroperoxides [4].
See Tetramethyl-1,2-dioxetane
See other CYCLIC PEROXIDES, STRAINED-RING COMPOUNDS

DropBooks

DIOXYGENYL POLYFLUOROSALTS **$O_2^+[MF_n]$ or O_2^+ $[EF_n]$**

1. Bailar, 1973, Vol. 2, 778−779
2. Griffiths, J. E. *et al., Spectrochim. Acta*, 1975, **31A**, 1208

Dioxygenyl hexafluoro-antimonate, -arsenate, -phosphate, -platinate and -stannate, also tetrafluoroborate, all react very violently with water, liberating ozone and oxygen [1]. Irradiation for Raman spectroscopy of a range of the title compounds and their nitrosyl analogues in glass or quartz capillaries caused many of them to decompose explosively. A special rotating sapphire/Teflon cell overcame the problem. Compounds examined were dioxygenyl hexafluoro-arsenate, -bismuthate, -ruthenate, -rhodate, -platinate and -aurate; dioxygenyl undecafluorodi-antimonate, -niobate and -tantalate; and their nitrosyl analogues [2].
See other IRRADIATION DECOMPOSITION INCIDENTS

DIPHENYL BLACK

Anon., *Loss Prev. Bull.*, 1980, (030), 160

A batch of the trisazo dyestuff, after drying at 100–105°C in a circulating air dryer, was left in the unheated dryer overnight. Exothermic decomposition set in after some hours.

See other AZO COMPOUNDS

DIPLUMBANES **R_3PbPbR_3**

Sidgwick, 1950, 595

The higher members of the hexaalkyldiplumbane series may disproportionate explosively during distillation.

See other ALKYLMETALS

1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES

Anderson, J. R. *et al., J. Org. Chem.*, 1975, **40**, 2016

Several substituted title salts, intermediates in the preparation of 1,3-diselenole-2-selenones, exploded on heating, ignition or shock. The tetrafluoroborate salts were stable, safe intermediates for large-scale application. Individually indexed compounds are:

1-(4,5-Dimethyl-1,3-diselenonylidene)piperidinium perchlorate, 3340

2-(1,3-Diselena-4,5,6,7-tetrahydroindanylidene)piperidinium perchlorate, 3408

1-(4-Methyl-1,3-diselenonylidene)piperidinium perchlorate, 3174

1-(4-Phenyl-1,3-diselenonylidene)piperidinium perchlorate, 3659

See other OXOSALTS OF NITROGENOUS BASES

DISPOSAL

1. *Hazardous Chemicals: Information and Disposal Guide*, Armour, M. A. *et al.*, Edmonton, University of Alberta, 1984
   Handbook of Laboratory Waste Disposal, Pitt, E. & M. J., Chichester (UK), Ellis Horwood, 1985.
2. Chivers, G. E., *Disposal of Hazardous Wastes*, Northwood (Mdx.), Science Reviews Ltd., 1983
3. *Hazardous and Toxic Materials: Safe Handling & Disposal*, Fawcett, H. H., New York, Wiley, 1984
4. *The Disposal of Hazardous Waste from Laboratories*, Proceedings of RSC Chemical Information Group meeting, March 1983, London, RSC, 1983
5. Voegelein, J. F., *J. Chem. Educ.*, 1966, **43**, A151–157
6. Teske, J. W., *J. Chem. Educ.*, 1970, **47**, A291–295
7. Allen, R. O., *J. Chem. Educ.*, 1983, **60**(3), A814
8. Cook, J. D., reference 4 above, 116
9. Ghosh, P. K. *et al., Proc. 11th Int. Sympos. Prev. Occup. Risks Chem. Ind.*, 703–719, Heidelberg, ISSA, 1987

The gap left in the literature on disposal of hazardous laboratory materials by the withdrawal in 1980 of the MCA manual has been filled adequately by new compilations. In addition to providing brief details on general properties, reactive and toxic hazards for each of some 300 laboratory chemicals, detailed directions for

disposal of spills, residues or package lots are available. Disposal methods have been laboratory tested for completeness of reaction, safety and practical utility [1]. All aspects of the implications and operation of UK hazardous waste legislation and the derived practical systems are covered in a 100 page survey, which includes a chapter on disposal of wastes from chemical, biological and radiochemical laboratories [2]. The third reference is concerned more with the long-term implications of past and previous large-scale disposal procedures than with the practical detail of laboratory disposal methods [3]. Many aspects of the complex problems and practical solutions related to disposal of laboratory wastes were covered comprehensively in a symposium [4]. Practical solutions to disposal problems adopted by an explosives research laboratory [5], and by two American universities have been described [6,7], the former including details on the use of explosives to rupture corroded and unusable cylinders of compressed or liquefied gases.

Some of the techniques employed need a remote area for safe operations, which may not be available to laboratories in urban locations. In such cases the services of a specialist chemical disposal contractor may be the most practical solution. It is, however, possible to minimise disposal problems by strict control on quantities ordered for stock (resisting bargain bulk offers), and on stockroom procedures. The reasons for the reluctance of many practising chemists to accept the fact that they are, almost invariably, the person best qualified to deal at the point of origin with difficult or dangerous residues were discussed [8]. Problems encountered and their solutions in disposing of inventories after a chlorine leak in a disused chemical factory are discussed. A large spill of liquid chlorine was largely absorbed in sodium hydroxide. Vinyl chloride was pumped out and removed, hydrogen was released slowly to atmosphere and acetylene was flared off [9].

DropBooks

1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE SALTS

Preparative hazard

See Carbon disulfide: Alkali metals

DRUMS

Several accidents in this book, some fatal, involve bursting forty-five gallon (215 litre, 55 gallon US) steel drums, a standard chemical packaging. These are sometimes attributed to setting off an explosion in the headspace of a bulging drum while attempting to vent it. In fact, a bulging drum can contain quite enough mechanical energy to kill, cut pipelines, etc. A bulging drum will eventually burst unattended, but the last straw, which breaks the worker's neck if he is in the wrong position, may be the slight additional stress of handling. The most damage results when the bottom blows out, this creates what, in military terms, is a spigot mortar, allowing the compressed gas in the headspace to transfer most of its energy to the bulk of the drum. Since the bottom is under more stress, both chemical and physical, than the top, having the weight of the contents as well as the gas pressure to resist, such failure is probable in a symmetric drum. Any worker standing above the drum while trying to vent it may then be struck hard beneath the chin by 15 kg

of percussive instrument travelling at modest speed — result a broken neck. Do not stand above bulging drums when trying to vent them. The relatively light, if sharp edged, top plate, though accelerated over a very short distance before the gas vents, is still dangerous. Chemists must beware of storing materials which can either generate gas, react with the drum to produce hydrogen, or be catalysed by it to self-heat to boiling.

See STEEL:apricots

DRYING

1. *High Vacuum Techniques for Chemical Syntheses and Measurements*, Plesch, P. H., Cambridge, Cambridge University Press, 1989, pp. 140, 141
2. *Purification of Laboratory Chemicals*, Perrin, D. D., Armarego, W. L. F. (Eds.), New York, Pergamon, 3rd edn.
3. *Drying: Principles and Practice*, Keey, R. B., Oxford, Pergamon, 1972
4. *Spray Drying Handbook*, Masters, K., Harlow (Essex), Longmans, 5th edn. 1992
5. *Industrial Drying Equipment Selection and Application*, van't Land, New York, Marcel Dekker, 1991

In the strict chemical sense, the term drying refers to removal of water present in solid or fluid materials by treatment with water-reactive chemicals. In a wider (chemical engineering) context, it also refers to use of physical methods to remove any unwanted liquids (or vapours) from solid, liquid or gaseous phases.

The first reference is largely devoted to small scale and intensive drying of solvents and reagents by chemical methods for use in kinetic work. Chemical drying is commonly a source of hazard since the reagents used are, of their nature, often extremely reactive, and not only with water; a discussion of hazards is given [1]. A good example of such an agent is magnesium perchlorate (Anhydrone) which reacts with a variety of chemicals or solvents to form explosive products or adducts. Generally its use should be avoided. The next reference covers various aspects of laboratory scale purification and possibly less rigorous drying of a wider range of materials [2]. The remaining references cover chemical engineering aspects of industrial drying operations, with attention to safety aspects [3,4,5].

Drying, usually by physical methods, is one of the most common unit operations in both laboratory or industrial scale process chemistry, and since heating is usually employed to remove volatiles, thermally unstable materials may decompose if overheated. As a light-hearted example, when a faulty oven thermostat led to overheating of mercuric thiocyanate, a monstrous 'Pharaoh's serpent' resulted. Drying moist cadmium propionate in an electric oven led to explosive ignition of the diethyl ketone vapour produced as an unforeseen by-product. Drying 3,5-dinitro-2-toluamide had more serious consequences.

Chemical drying of liquids often involves reaction, with or without heating, of a solid which will react selectively with water. Calcium or lithium aluminium hydrides are often used; evolved hydrogen needs safe venting. For the lithal, careful stirring and temperature control is essential to prevent formation of extremely

reactive aluminium, which may react violently with oxygenated or halogenated solvents like dioxan or trichloroethane.

When adsorbents are used to dry gases or liquids, often in a flow system, the adsorbents may need pre- or post-treatment to avoid hazards. Thus, when ethylene was contacted with molecular sieve not previously treated with dilute ethylene, the adsorption exotherm heated the bed to red heat and ruptured the drier. When peroxide-containing ethers are simultaneously dried and purified by chromatography (passage through an alumina column), the peroxides are concentrated on the alumina, which must be treated before disposal.

The drying of solids may involve the removal of volatile solvents. When these are flammable, ignition sources must be excluded to minimise risk of fire or explosion.

Some industrial drying techniques have inherent potential hazards. The conditions prevalent in spray drying, where a solution is sprayed into a hot gas (usually air), are likely to cause electrostatic charge generation, and stringent earthing/bonding precautions are necessary for flammable solvents or combustible solutes such as milk powder. Fluidised-bed driers may show similar problems with dusty organic materials, and gas-inerting is desirable.

There are unusual hazards associated with partial desolvation of crystalline solvated oxosalts, notably perchlorates. This may be because desolvation causes the oxygen balance to approach the zero balance point and maximum energy release potential. A similar effect has also been seen with an hydrated salt.

These and other examples may be found in the entries:

METAL–HALOCARBON INCIDENTS, (references 2, 3)
MILK POWDER
MOLECULAR SIEVE INCIDENTS: ethylene
ORGANIC POWDER HANDLING
PEROXIDES IN SOLVENTS
SOLVATED OXOSALT INCIDENTS
Cadmium propionate, 2418
Calcium acetylide: Methanol
Diazomethane: Calcium sulfate, 0406
3,5-Dinitrotoluamide
Lithium tetrahydroaluminate: Dioxane, 0075
Magnesium: Methanol, 4690
Magnesium perchlorate, 4084
Mercury(II) thiocyanate, 0979
Silicon dioxide: Hydrochloric acid
Sodium: Halocarbons (reference 10)
Sodium azide Heavy metals, 4758
Sulfuric acid: Hydrofluoric acid, 4479
Vinyl acetate: Desiccants, 1532

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS
See also FLASH POINTS
See other UNIT OPERATIONS AND PROCESSES

DropBooks

DUST EXPLOSION INCIDENTS

1. Dorsett, H. G. *et al., Rept. RI 7132*, Washington, US Bur. Mines, 1968
2. Hartmann, I., *Ind. Eng. Chem.*, 1948, **40**, 752
3. Palmer, K. N., *Dust Explosions and Fires*, London, Chapman & Hall, 1973
4. Nagy, J. *et al., Rept. BM-RI 7208*, Washington, USAEC, 1968
5. Yowell, R. L. *et al., Loss Prev.*, 1968, **2**, 29–53
6. Strizhevskii, I. *et al., Chem. Abs.*, 1975, **82**, 6147
7. Griffiths, W. C., *Ann. Rev. Fluid Mech.*, 1978, **10**, 93–105
8. Cardillo, P. *et al., Dust Explosions & Fires: Guide to Literature*, Milan, Staz. Sperim. Combust., 1979
9. Moore, P., *Chem., & Ind.*, 1979, 430–434
10. Pomeranstsev, V. V. *et al., Chem. Abs.*, 1979, **91**, 7257
11. Field. P., *Handbook of Powder Technol., Vol. 4, Dust Explosions*, Amsterdam, Elsevier. 1981
12. Eckhoff, R. K. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom.* Process Ind., Vol. 3, F11–20, Rugby, IChE, 1983
13. Fusamura, N. *et al., Chem. Abs.*, 1983, **98**, 5957
14. *Dust Explosions: Combustible Particles and Control*, PB84-878073, Richmond (Va.), USNTIS, 1984
15. Radsziszewska, J. M., *Arch. Combust.*, 1986, **6**, 139–149
16. Enright, R. J., *Chem. Abs.*, 1987, **106**, 125260; **110**, 120443h
17. Sweis, F. K., *J. Haz. Mat.*, 1987, **14**, 241–246
18. Lunn, G., *Inf. Chim* . (Fr.), 1986, **278**, 225–230
19. Moore, P. E., *EuropEx Newsl.*, 1987, (4), 2–4
20. Moore, P. E. *et al., Staub-Reinhalt. Luft*, 1987, **47**(7–8), 207–213
21. Weckman, H., *Fire Saf. J.*, 1987, **12**(2), 97–102
22. Grossel, S. S., *J. Loss Prev. Proc. Ind.*, 1988, **1**, 62–74
23. *ASTM Spec. Tech. Publ. 958*, Industrial Dust Explosions, Cashdollar, K. L., Hertzberg, M. (eds), Philadelphia, ASTM, 1987, 191–201
24. Lunn, G. A., *J. Haz. Mat.*, 1988, **17**, 207–213
25. Aglan, H., *Part. Sci. Technol.*, 1988, **6**, 43–51
26. Lee, J. H. S. *et al., Arch. Combust.*, 1987, **7**, 279–297
27. Bartknecht, W., *Staub* — Reinheit. Luft, 1988, **48**(10), 354–368; (11), 417–425
28. Dehn, C. J., *Arch. Combust.*, 1987, **7**(3–4), 299–312
29. Amyotte, P. R. *et al., J. Loss Prev. Proc. Ind.*, 1989, **2**, 87–94
30. Radziszewska, J. M., *Arch. Combust.*, 1987, **7**, 315–320
31. Matsuda, T., *Arch. Combust.*, 1987, **7**, 237–253
32. Jarosinski, J. *et al., Arch. Combust.*, 1987, **7**, 267–278
33. Fangrat, J. *et al., Arch. Combust.*, 1987, **7**, 321–332
34. Abbot, J. A., *EuropEx Newsl.*, 1988, (8), 4–10
35. Eckhoff, R. K., *Dust Explosions in the Process Industries*, Oxford, Butterworth-Heinemann, 1991
36. Proc. 6th Int. Colloq. Dust Expl., Deng, X., Wolanski, P. (Eds.), Shenyang China, Northeast. Univ. Press, 1994.
37. Plewinsky, B. *et al., Prax. Sicherheitstech.*, 1997, **4**, 95

Laboratory dust explosion data were presented for 73 chemical compounds, 29 drugs, 27 dyes and 46 pesticides, including ignition temperatures of clouds and layers, minimum ignition energy, explosion-limiting concentrations and pressures, and rates of rise at various dust concentrations. Explosibility indices were computed where possible and variation of explosibility parameters with chemical composition was discussed. General means of minimising dust explosion hazards were reviewed [1]. Of the 17 dusts investigated earlier, the 4 metals examined — aluminium, magnesium, titanium and zirconium — were among the most hazardous. Aluminium and magnesium show the maximum rates of pressure rise and final pressures, magnesium having a low minimum explosive concentration. Ignition of zirconium dust often occurred spontaneously, apparently owing to static electric discharges, and undispersed layers of the dust could be ignited by less than 1μJ compared with 15μJ for a dispersed dust. All except aluminium ignite in carbon dioxide atmospheres [2]. A comprehensive account of practical and theoretical aspects of laboratory and plant-scale dust explosions and fires includes appended tabulated data for over 300 dusts of industrial significance [3]. Laboratory dust explosion data for 181 miscellaneous hazardous materials and 88 non-hazardous materials are presented [4]. Papers and symposium discussions on several aspects of the topic were presented [5], together with further data on dust-explosivity of several metallic and non-metallic industrial materials [6]. A comprehensive survey of the whole field has recently (1991) been published [35].

A review including fluid mechanical considerations and useful applications among other aspects of dust explosions [7], and a collection of abstracts covering 20 years to 1977 [8] have been published. In a comparative study of laboratory methods available for assessing dust explosibility, the influence of ignition source type and containing vessel size are discussed in detail [9]. Spontaneous combustion and explosion of natural fuel dusts are covered [10], and a new text on the topic is available [11]. The ultimate experiments in dust explosion research in full size 500 m^3 silos using wheat grain, soya meal and maize starch dusts have been described [12]. Explosions of dispersed 200 mesh cellulose dust was inhibited by presence of potassium chloride, lead nitrate and cadmium sulfate, but promoted by barium chloride or potassium nitrate above 1.3% conc. [13]. A new bibliography (163 entries, 1970–84) cites dust generated explosion details in various industrial environments, particularly agricultural, and classifies combustible dusts [14]. An extensive series of papers on many aspects of dust explosions are collected in [36].

The lower explosive limit and minimum explosive concentrations of flax, wool, cotton, jute, hemp and sisal fibres are of the same order of magnitude as those of highly explosive dusts [15]. The explosibility of pyrites dusts with sulfur contents above 20% was evaluated experimentally. Dusts of 30% sulfur content gave explosion pressures of 3 bar at pressure rise rates of 16 bar/sec. Mixtures of 60% pyrites and 40% powdered limestone still showed significant pressure effects, and the proportion of limestone actually needed to suppress explosions was considerably above the values currently accepted by mining industries [16]. Effects of mixtures of particle sizes in combustible dusts upon minimum ignition temperature (T_i^m) and upon presence or absence of explosion were studied. Presence of 30% of fines in a coarse dust lowers T_i^m significantly [17]. Experimental explosions of polyethylene,

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phenolic resin, dye, and aspirin powders demonstrated the resistance to explosion of an industrial dust collector fitted with automatic explosion relief panels [18]. The validity of suppressing dust explosions in volumes up to 1000 m^3 using a few large suppressors has been established [19], and the efficacy of the system was proven in an experimental spherical vessel 6.3 m in diameter [20]. The maximum explosion pressures for relatively fine and dry peat dusts may be estimated with a fair degree of accuracy from the moisture content, provided that the mean particle size is below 200μm and that the moisture content is below 35%. For coarser and moister peat dusts, it may only be possible to assess whether it is explosive, and inhomogeneity in peat samples causes further significant problems [21].

In a comprehensive review of dust explosion problems and hazards associated with mechanical handling systems (pneumatic, screw, and belt conveyors, bucket elevators, en masse conveyors) for bulk transfer of a wide variety of solid chemicals and industrial materials, tabulated data for some 400 such materials are presented. The data are given under the headings minimum ignition temperatures, explosible concentrations in air, and ignition energies; and maximum explosion pressures, rates of pressure rise, and oxygen concentrations to prevent ignition. Of these 400 materials, 33 are notable in that the maximum rates of pressure rise observed exceed 680 bar/s (10,000 psi/s). Figures below for these 33 materials are for maximum explosion pressure (bar) and maximum rate of rise (bar/s), respectively, except where noted.

Acetoacet-4-phenetidide, 5.9, 680; atomised aluminium, 5.7, >1.36 kbar/s; aluminium flake, 8.6, >1.36 kbar/s; aluminium–cobalt alloy, 6.25, 748; aluminium–magnesium alloy, 5.85, 680; aluminium–nickel alloy, 6.5, 680; aluminium stearate, 5.85, 680; benzoic acid, 6.85, 700; 2,2-bis(4-hydroxyphenyl) propane, 5.5, 803; calcium silicide, 5.85, 1.36 kbar/s; calcium stearate, 6.6, >680; cellulose nitrate, >17.4, >1.42 kbar/s; 2-chlorobenzylidenemalononitrile, 6.1, >680; coumarone–indene resin, 6.3, 748.

1,4-Diaminobenzene, 6.4, 748; 2,6-di-*tert*-butyl-4-cresol, 5.4, 884; dimethyl terephthalate, 7.1, 816; 3,3'-dimethoxy-4,4′-diaminobiphenyl, 5.6, 680; 3,5-dinitrotoluamide, 10.4, 680; 1,3-diphenyltriazene, 7.75, >680; 2,4-hexadienoic acid, 7.2, >680; hexamethylenetetramine, 6.7, 748; magnesium, 7.9, 884; paraformaldehyde, 9.0, 884; phytosterols, 5.2, >680; poly(acrylonitrile), 6.0, 748; rosin, 5.7, 816; silicon, 6.4, 884; tetraphosphorus decasulfide, 4.35, >680; thorium hydride, 5.5, 816; titanium, 5.8, 816; titanium hydride, 8.2, 816; zinc stearate, 5.4, >680; zirconium, 5.1 bar, 740 bar/s [22]. In the proceedings of the 1986 Pittsburgh conference on dust explosions, many aspects of the occurrence, prevention and protection from the effects of industrial dust explosions involving a wide variety of materials are presented in a series of papers [23].

Lower limits of explosibility of several organic dusts were determined and found to be in general agreement with estimated values [24]. Probabalistic aspects of occurrence of dust explosions were studied experimentally with lycopodium powder in relation to dust and hot surface (or dust) temperature. The probability of explosion increases with dust concentration, then falls off, due to the ballast effect of unburnt dust. Probability also increases continuously with the temperature of the hot surface and/or dust particles. Application of the results to practical plant

installations is discussed [25]. The effect of turbulence (which increases degree of dispersion and reduces the rate of settlement) on closed-volume explosions of dust–air mixtures has been studied [26]. In a 2 part publication, test methods and derived parameters, and preventive and protective measures are reviewed in relation to explosions in combustible dusts and in their mixtures [27]. A method has been described to assess the effect on explosion energy of presence of low concentrations of flammable vapours in dust–air mixtures in a 20 l chamber. Significant increases in rate of pressure rise were observed in corn starch–air mixtures with added refuse-derived fuel vapour [28]. The effect of turbulence on explosion parameters of lycopodium dust in a 1.2 l Hartmann bomb has been studied in two parallel series of experiments. One series in the bomb gave relation between dispersing air pressure, dust concentration, ignition delay time and the maximum rate of pressure rise. A second series in a plexiglass version of the bomb (without ignition) showed the relation beteen dispersing air pressure and dust velocity (measured by laser Doppler velocimeter) and settling time. The decay of turbulence in the Hartmann bomb is rapid (below 200 ms), and this time frame coincided closely with the rapid fall off in the rate of pressure rise with ignition delays of 40–180 ms. The correlation depends on dust concentration and dispersing air pressure [29]. The explosive behaviour of mixtures of flax dust and fibres with air has been studied [30]. The influence of air velocity upon ignition and flame propagation in dust–air mixtures under pneumatic tube conveyor conditions has been studied [31]. Minimum quenching distances for control of dusts of cornstarch, aluminium and coal have been determined [32], and flame propagation and transition to detonation has been studied in mixtures of organic dusts with oxygen-enriched air [33]. A survey of dust fires and explosions in UK during 1979–84 revealed that dusts most frequently involved were those of grains and cereals, animal feeds and food products, while wood and metal dusts were often involved. Other dusts involved were sulfur, phosphorus trisulfide, zinc phosphide, carbon and rubber. Losses from dust fires were more common than from dust explosions [34].

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Mist explosions are, of course, dust explosions in which the particles happen to be liquid. Other less common types of detonation involving gaseous oxidants are reviewed in [37]. These include wick explosions, foam explosions, and surface explosions.

See METAL SULFIDES, FLOUR

See also GEOMETRY OF VESSELS AND PIPEWORK, DEFLAGRATION TO DETONATION

Methane

Reeh, D., *Chem. Abs.*, 1979, **90**, 126799

Tests on the explosive behaviour of combustible dust–methane–air mixtures in a 45 mm pipeline 200 m long showed that presence of a little fuel gas could cause combustible but non-explosive dusts to become unexpectedly hazardous.

See CARBONACEOUS DUSTS, DUSTS, METAL DUSTS

Individually indexed incidents include:

Acetoacet-4-phenetidide, 3529

O-Acetylsalicylic acid, 3137
Aluminium, 0048
Aluminium–cobalt alloy, 0049
Aluminium–magnesium alloy, 0053
Aluminium stearate, 3914
Benzoic acid, 2732
2,2-Bis(4-hydroxyphenyl)propane, 3686
Calcium silicide, 3943
Calcium stearate, 3896
2-Chlorobenzylidenemalononitrile, 3333
1,4-Diaminobenzene, 2371
2,6-Di-*tert*-butyl-4-cresol, 3691
3,3′-Dimethoxy-4,4′-diaminobiphenyl, 3660
Dimethyl terephthalate, 3292
3,5-Dinitro-2-toluamide, 2941
1,3-Diphenyltriazene, 3506
2,4-Hexadienoic acid, 2385
Hexamethylenetetramine, 2477
Magnesium, 4690
Magnesium–nickel hydride, 4464
Paraformaldehyde, 0417
Poly(ethylene), 0782
Silicon, 4909
Sucrose, 3558
Tetraphosphorus decasulfide, 4878
Thorium dihydride, 4489
Titanium, 4919
Titanium carbide, 0561
Titanium dihydride, 4490
Zinc stearate, 3897
Zirconium, 4928

DUSTS

1. Taubkin, S. I. *et al.*, *Chem. Abs.*, 1976, **85**, 110611
2. Leuschke, G., *Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 2, 647–656, Basle, SSCI, 1980
3. *NFPA 654*, Quincy (Ma), National Fire Protection Association, 1988

A new method of classifying hazardous dusts into the 3 groups, highly explosible, explosible and fire-hazardous was proposed, based on lower explosive limits and maximum rate of pressure increase. An extension of the system to classify work-rooms taking account of their volumes was also suggested [1]. The dependency of induction time (time until critical self-heating occurs) upon storage temperature and volume of dusts stored at or above their ignition temperatures has been studied [2]. A new US fire code covers prevention and control of fires and dust explosions in the chemical, dyestuffs, pharmaceutical and plastics industries [3].

EARTHQUAKE

Pine, S. H., *Chem. Health & Safety*, 1994, **1**(2), 10.

A discussion, based on experience, of the measures needed to protect laboratories and equipment in earthquake zones.

Earthquakes provide the ultimate test of the storage of incompatible chemicals and are sometimes followed by fires in chemical stores. Very few causes of ignition are found: alkali metals; halogen oxysalts in conjunction with strong acids; and sulphuric or nitric acid and cellulose (wood flooring). These usually then ignite vapours of flammable solvents.

See STORAGE OF CHEMICALS

ELECTRIC FIELDS

Kabanov, A. A. *et al., Russ. Chem. Rev.*, 1975, **44**, 538–551

Application of electric fields to various explosive heavy metal derivatives (silver oxalate, barium, copper, lead, silver or thallium azides, or silver acetylide) accelerates the rate of thermal decomposition. Possible mechanisms are discussed.

ELECTROLYSIS

Mason, J. P., personal communication, 1999

Electrolysis is a means of putting energy into a chemical system. That energy may be stored in the system, to emerge spontaneously later. Apparently innocuous systems can thereby become extremely hazardous. The obvious example is the cleavage of water to produce an explosive mix of hydrogen and oxygen. There are more subtle risks: the performance of an electrode design was being tested over several weeks in a solution of ammonium chloride, topped up daily with ammonia. After about three weeks, the technician who topped up the beaker containing the assembly found its contents flying past his ears. No substantial piece of the beaker was ever found. That was trichloroamine formation, and destruction. Other nitrogenous compounds, in other halide electrolytes, could behave similarly.

See Ammonium chloride, Deuterium oxide

See also BATTERIES

DronaBrooks

ELECTRON BEAM MELTING

Brinza, V. N. *et al., Chem Abs.*, 1987, **106**, 22657

Potential hazards associated with electron beam vacuum melting of metals include the possibility of ignition of metal aerosols or condensate films in the event of sudden loss of vacuum at elevated temperatures.

ELECTROSTATIC HAZARDS

1. Haase, H., *Electrostatic Hazards: Evaluation and Control*, Weinheim, Verlag Chemie, 1977
2. Anon., *Loss Prev. Bull.*, 1979, (029), 134–138
3. Anon., *CISHC Chem. Safety Summ.*, 1980, **51**, 4–6

4. Anon., *Loss Prev. Bull.*, 1980, (035), 1–5
5. Maksimov, B. K. *et al.*, *Chem. Abs.*, 1982, **96**, 165336
6. Anon., *Jahresber.*, 1985, 70–72
7. Wilson, N., *Chem. Abs.*, 1986, **105**, 138978
8. Jury, E., *Safety aspects and measures in electrostatic gas purification*, DECHEMA Monogr. 107, 1987, 383–388
9. Pay, F. J., *Loss Prev. Bull.*, 1987 (078), 1–8
10. Cartwright, P., *Chem. Engr.* (Rugby), 1988, (454), 49
11. Pratt, T. H., *Process Safety Progr.*, 1993, **12**(4), 203

The comprehensive text contains numerous case studies and quantitative calculations on many aspects of static electrical hazards [1]. Case histories involving leakage of steam or other pressurised fluid, flow to or from storage tanks, dusts and unearthed plant segments are discussed [2]. In a group of 7 incidents involving fire or explosion, the common ignition source was static generated by pouring fine solids from plastic bags or through non-conducting ducts or funnels [3]. Seven further case histories involving fires or explosions in dusts or powders under various circumstances are detailed [4]. Equations for calculating maximum flow rates to avoid static build up during transfer of petroleum products to or from road or rail tanks have been derived [5].

In the preparations during unsettled weather for a large outdoor firework display, the pyrotechnic components, together with the starting fuses, electric igniters and charged batteries were all stored in the same building. The batteries were to be protected from the weather by wrapping in polythene film, and when this was unreeled, static discharge led to ignition of the stored materials, and uncontrolled fires and explosions destroyed the building [6]. Factors affecting incendiary behaviour of static spark discharges from the human body on ignition of methane–and hydrogen–air mixtures are discussed [7]. Safety aspects and precautionary measures to prevent fire and explosion in electrostatic gas purifiers are discussed [8]. A brief survey of the phenomenon, consequences and hazards of electrostatic charging in industrial operations is illustrated by case histories [9]. Accidents originating from static charge generation during the pouring of powder from polythene-lined fibreboard drums, or when digging dry cake from a vacuum filter bed dryer are analysed, and preventive measures proposed [10]. Poorly designed fire extinguishing systems may also lead to static hazards. A specialised mechanism for ignition of oxygen-rich atmospheres by electrostatic effects generated by bursting oxygen bubbles from decomposing hydrogen peroxide is postulated [11].

See Carbon dioxide: Flammable materials
See other IGNITION SOURCES

ENDOTHERMIC COMPOUNDS

1. Weast, 1979, D61–84
2. Mellor, 1941, Vol. 1, 706–707
3. Stull, 1977, 8–10

Most chemical reactions are exothermic, but indirect or high temperature reactions permit preparation of high energy product(s) which are known as endothermic

(or energy-rich) compounds. Such compounds are thermodynamically unstable, because heat would be released on decomposition to their elements. The majority of endothermic compounds possess a tendency towards instability and possibly to explosive decomposition under various circumstances of initiation. Often, endothermic compounds possess features of multiple bonding ('unsaturation'), as in acetylene, hydrogen cyanide, silver fulminate, mercury azide or chlorine dioxide. Other singly bonded endothermic compounds are hydrazine, diborane, dichlorine monoxide, or nitrogen trichloride.

Many, but not all, endothermic compounds have been involved in violent decompositions, reactions or explosions, and in general, compounds with significantly positive values of standard heat of formation may be considered suspect on stability grounds. Notable exceptions are benzene and toluene (ΔH°_{f} +82.2, 50.0 kJ/mol; 1.04, 0.54 kJ/g, respectively), where there is the resonance stabilising effect of aromaticity. Values of thermodynamic constants for elements and compounds are tabulated conveniently [1], but it should be noted that endothermicity may change to exothermicity with increase in temperature [2]. There is a more extended account of the implications of endothermic compounds and energy release in the context of fire and explosion hazards [3]. Many examples of endothermic compounds will be found in the groups:

See also ACETYLENIC COMPOUNDS, ALKYLMETALS, ALKYNES, AZIDES, BORANES, CYANO COMPOUNDS, DIENES, HALOACETYLENE DERIVATIVES, HALOGEN OXIDES, METAL ACETYLIDES, METAL FULMINATES, OXIDES OF NITROGEN

The individually indexed endothermic compounds, for most of which heats of formation are given in the text:

† Acetonitrile, 0758
∗ Ammonium hexacyanoferrate(II), 2577
† Arsine, 0100
Azido-2-butyne, 1473
3-Azidopropyne, 1114
cis-Azobenzene, 3484
Azoxybenzene, 3485
Barium azide, 0214
Benzenediazonium nitrate, 2275
Benzotriazole, 2269
Borane, 0135
Bromine azide, 0256
† 3-Bromopropyne, 1090
† 1,2-Butadiene, 1479
† 1,3-Butadiene, 1480
† Buten-3-yne, 1423
† 1-Butyne, 1481
† 2-Butyne, 1482
Cadmium azide, 3957
Cadmium cyanide, 0588
Cadmium fulminate, 0589
Cadmium nitride, 3960

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Calcium azide, 3936
† Carbon disulfide, 0560
Chlorine dioxide, 4042
Chloroacetylene, 0652
Chloryl perchlorate, 4104
Copper(I) azide, 4287
Cyanamide, 0404
Cyanoform, 1383
Cyanogen bromide, 0313
Cyanogen chloride, 0323
Cyanogen fluoride, 0323
3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-) oxide, 2630
† Cyclopropane, 1197
Diazene, 4469
2,3-Diazido-1,3-butadiene, 1437
Diazomethane, 0406
† Diborane(6), 0166
Dichlorine oxide, 4095
Dichlorine trioxide, 4100
† Dicyanoacetylene, 1801
1,4-Dicyano-2-butene, 2311
Dicyanofurazan, 1803
Dicyanofurazan *N*-oxide, 1804
† Dicyanogen, 0996
Diethylcadmium, 1677
Difluorodiazene, 4314
Diiodomethane, 0400
Dimethylcadmium, 0894
Dimethylmercury, 0907
Dimethylzinc, 0935
Dinitrogen oxide, 4744
Dinitrogen tetraoxide, 4747
Dioxygen difluoride, 4320
∗ *trans*-1,2-Diphenylethylene, 3643
Fluoroacetylene, 0662
Gold(III) oxide, 0115
1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1,3,5-triphosphorine, 4795
Hydrogen azide, 4441
† Hydrogen selenide, 4486
† Hydrogen telluride, 4488
Iodoform, 0376
Lead(II) azide, 4782
Lead(IV) azide, 4790
Mercury(II) cyanide, 0976
Mercury(II) fulminate, 0978
∗ Mercury(II) thiocyanate, 0979

† 2-Methyl-1,3-butadiene, 1893
† 3-Methyl-1,2-butadiene, 1892
† 3-Methyl-1-butyne, 1894
∗ Methyl isocyanide, 0759
Nickel(II) cyanide, 0997
Nitrogen oxide, 4724
Nitrogen trichloride, 4143
Nitrosyl chloride, 4023
Nitrogen triodide, 4633
Nitryl chloride, 4025
Nitryl hypofluorite, 4304
Oxygen difluoride, 4317
† Pentaborane(9), 0188
† 1,2-Pentadiene, 1895
† 1,3-Pentadiene, 1896
† 1,4-Pentadiene, 1897
† 1-Pentyne, 1898
† 2-Pentyne, 1899
Perchloryl perchlorate, 4107
† Phosphine, 4508
∗ Phosphorus triazide oxide, 4788
Potassium hexacyanoferrate(III), : Hydrochloric acid, 4242
† Propadiene, 1124
Propadienedithione, 1350
† Propyne, 1125
Silicon tetraazide, 4791
Silver azide, 0023
Silver cyanide, 0299
Silver fulminate, 0301
∗ Sodium hexaazidophosphate, 4794
† Stibine, 4510
Strontium azide, 4785
Styrene, 2945
Tetracyanoethylene, 2629
Tetraethyllead, 3095
Tetramethyl-2-tetrazene, 1759
Tetrasulfur tetranitride, 4770
∗ Tetravinyllead, 3016
Tetrazole, 0411
∗ Thallium(I) tetraazidothallate, 4792
∗ 2,4,6-Trichloro-1,3,5-triazine, 1038
∗ Vinyl isocyanide, 1109
Zinc cyanide, 1004

DropBooks

ENERGETIC COMPOUNDS

1. Witucki, E. F. *et al., J. Chem. Eng. Data*, 1983, **28**, 285–286
2. Various, *Mater. Res. Soc. Proc.* (418), 1996

Syntheses of 5 energetic aliphatic azido compounds are described: caution is necessary in handling these because of their impact-sensitivity [1]. A later symposium on energetic materials, here meaning explosives and popellants, is reported [2]. Individual compounds are:

6-Azidohexyl 6-azidohexanoate, 3551

Bis(2-azidoethoxymethyl)nitramine, 2481

N-Butyl-*N*-2-azidoethylnitramine, 2528

1,12-Diazido-3,10-dioxa-5,8-dinitrazadodecane, 3049

Tris(2-azidoethyl)amine, 2482

See also ENDOTHERMIC COMPOUNDS, FLUORODINITROMETHYL COMPOUNDS (reference 6)

ENVIRONMENTALISM

1. Kletz, T. A., *Chemical Engineer*, 1992, 527, 38
2. Kletz, T. A., *Process Safety Progr.*, 1993, **12**(3), 147
3. Förster, H. *et al., Ber. Dtsch. Wiss. Ges.; Erdöl, Erdgas, Kohle Forschungsber.*, 1994, 462
4. De Haan, J. D. *et al., Proc. Int. Conf. Fire. Safety*, 1995, **20** 67

Environmentalists react violently to the mere word chemical. Some cases where Green and naive over-reaction has led to environmental damage and accompanying human fatalities from explosion are described and some likely causes of future mishap suggested [1,2]. It is proposed to lower the permitted vapour pressure of gasoline, to reduce environmental release of Volatile Organic Compounds, which will bring the headspace of car fuel tanks below the upper explosive limit on cool mornings [3]. Consideration is given to the increased fire risk of household aerosols associated with use of liquid petroleum gases and dimethyl ether as environmentally friendly propellants [4].

See Hydrogen peroxide: Waste treatment

EPOXIDATION

Swern, 1971, Vol. 2, 428–533

Preparation of epoxides (oxirans) on the commercial scale as resin or polymer components is widely practised. Careful control of conditions is necessary to avoid hazards, and the several factors involved are reviewed.

See Peroxyformic acid: Organic materials

Hydrogen peroxide: Unsaturated compounds, 4477

See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

1,2-EPOXIDES

Pogany, G. A., *Chem. & Ind.*, 1979, 16–21

All factors relevant to the safe use of ethylene oxide and propylene oxide in high pressure bench scale experiments are detailed. Salient points include the need for a well-designed agitated reactor with adequate provision for reaction heat removal and emergency pressure relief; prevention of back-flow from reactor to oxide storage vessels; avoidance of a reaction atmosphere of 100% ethylene oxide vapour and/or presence of air; avoiding an excess of oxide. The 3 lower members of this group of compounds are bulk industrial chemicals, and their high reactivity has been involved in several serious incidents.

Dinitrogen pentaoxide
See Dinitrogen pentaoxide: Strained-ring heterocycles

Nitronium perchlorate
See Nitronium perchlorate: 1,2-Epoxides

Individually indexed compounds are:
1-Allyloxy-2,3-epoxypropane, 2434
1,4-Bis(2,3-epoxypropoxy)butane, 3353
2,2-Bis[4(2′,3′-epoxypropoxy)phenyl]propane, 3825
† 1-Chloro-2,3-epoxypropane, 1162
† Cyclopentene oxide, 1906
2,3-Dibromo-5,6-epoxy-7,8-dioxabicyclo[2.2.2]octane, 2298
† 1,2:3,4-Diepoxybutane, 1507
† 1,2:3,4-Diepoxybutane, 1507
2,3:5,6-Diepoxy-7,8-dioxabicyclo[2.2.2]octane, 2339
Endrin, 3459
† 1,2-Epoxybutane, 1609
† 3,4-Epoxybutene, 1520
endo-2,3-Epoxy-7,8-dioxabicyclo[2.2.2]oct-5-ene, 2336
2,3-Epoxypropanol (Oxiranemethanol), 1229
2,3-Epoxypropionaldehyde 2,4-dinitrophenylhydrazone, 3130
2,3-Epoxypropionaldehyde oxime (Oxiranecarboxaldehyde oxime), 1182
4(2,3-Epoxypropoxy)butanol, 2866
∗ 2,3-Epoxypropyl nitrate, 1186
3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2403
† Ethylene oxide, 0829
† 1-Fluoro-2,3-epoxypropane, 1171
Glycidyl azide, 1191
Nitrilotris(oxiranemethane), 3181
† Propylene oxide, 4831
Tetrafluorooxirane, 0632
† Thiirane, 0840
1,3,5-Tris(2,3-epoxypropyl)triazine-2,4,6-trione, 3533
See other STRAINED-RING COMPOUNDS

DropBooks

EQUATIONS

Editor's comments

Balance them! The editor has frequently found chemists fresh from university blithely ignoring evolution of gaseous byproducts, such as carbon monoxide and methyl halides, capable of rupturing vessels and killing operators. Write them step by step too, this may reveal mechanistic and catalytic effects harmful to chemist, cost or yield.

See also NITRATION INCIDENTS

ETHERS

1. Jackson, H. L. *et al., J. Chem. Educ.*, 1970, **47**, A175
2. Davies, A. G., *J. R. Inst. Chem.*, 1956, **80**, 386–389
3. Dasler, W. A. *et al., Ind. Eng. Chem. (Anal. Ed.)*, 1946, **18**, 52
4. Hazardous Chemicals: Information and Disposal Guide, 1984, 87, 91, 98, 265
5. Robertson, R., *Chem. & Ind.*, 1933, **52**, 274
6. Morgan, G. T. *et al., Chem. & Ind.*, 1936, **55**, 421–422
7. Williams, E. C., *Chem. & Ind.*, 1936, **55**, 58–581
8. Karnojitsky, V. J., *Chim. et Ind.* (Paris), 1962, **88**, 233–238
9. Unpublished observations, 1973
10. Schwartz, A. M., *Chem. Eng. News*, 1978, **56**(24), 88

There is a long history of laboratory and plant fires and explosions involving the very high flammability and/or tendency to peroxide formation in these widely used solvents, diisopropyl ether being the most notorious. Methods of controlling peroxide hazards in the use of ethers have been reviewed [1], and information on storage, handling, purification [2,3] and disposal [4] have been detailed.

Three violent explosions of diisopropyl ether had been reported [5,6] and a general warning on the hazards of peroxidised ethers had been given by 1936 [7]. The latter reference mentions diethyl, ethyl *tert*-butyl, ethyl *tert*-pentyl and diisopropyl ethers as very hazardous, while methyl *tert*-alkyl ethers, lacking non-methyl hydrogen atoms adjacent to the ether link, are relatively safe. Bis(2-methyl-2-propen-1-yl) ether ('dimethallyl ether') is unusual in that although it forms peroxides with extreme rapidity, these are thermolabile and are progressively destroyed without danger during distillation [7]. For like reasons, the slower distillation enforced by industrial scale partly explains why peroxidation induced explosions are essentially laboratory accidents only. The mechanism of peroxidation of ethers has been reviewed [8].

When solvents have been freed from peroxides by percolation through a column of activated alumina, the adsorbed peroxides must promptly be desorbed by treatment with the polar solvents methanol or water, which should be discarded safely. Small columns used to deperoxidise diethyl ether or tetrahydrofuran were allowed to dry out by evaporation. When moved several days later, the peroxide concentrated on the alumina at the top of the columns exploded mildly and cracked the glass columns [9]. A procedure for preparation of dry oxygen- and peroxide-free low boiling ethers (diethyl ether, THF, dioxane, glyme etc.) is described which involves distillation from sodium diphenylketyl.

See Nitrogen oxide: Sodium diphenylketyl for care in disposal of the sodium–ketyl residues.

Individually indexed compounds include:

† Allyl ethyl ether, 1955
1-Allyloxy-2,3-epoxypropane, 2434
† Bis(2-ethoxyethyl) ether, 3076
Bis-(2-methoxyethyl) ether, 2549
† Butyl ethyl ether, 2540
1-(1,1-Dimethylethoxy)-2-methylpropane, 3072
† Butyl methyl ether, 2010
† *tert*-Butyl methyl ether, 2011
† Butyl vinyl ether, 2484
† Cyclopropyl methyl ether, 1608
† Diallyl ether, 2431
Dibenzyl ether, 3655
† Dibutyl ether, 3071
† 1,1-Diethoxyethane, 2545
† 1,2-Diethoxyethane, 2546
† 3,3-Diethoxypropene, 2858
† 2,3-Dihydrofuran, 1517
† Diisopropyl ether, 2542
† 1,1-Dimethoxyethane, 1700
† 1,2-Dimethoxyethane, 1701
† Dimethoxymethane, 1281
† 3,3-Dimethoxypropene, 1968
1-(1,1-Dimethylethoxy)-2-methylpropane, 3072
† 1,3-Dioxane, 1616
† 1,4-Dioxane, 1617
† Dipropyl ether, 2543
Di(2-propynyl) ether, 2327
† Divinyl ether, 1519
2-Ethoxyethanol, 1702
1-Ethoxy-2-propyne, 1909
† Ethyl isopropyl ether, 2012
† Ethyl propenyl ether, 1956
† Ethyl vinyl ether, 1610
† Furan, 1439
† Isopropyl vinyl ether, 1957
∗ Methoxy-1,3,5,7-cyclooctatetraene, 3149
2-Methoxyethanol, 1284
† 2-Methoxyethyl vinyl ether, 1973
† 2-Methyltetrahydrofuran, 1961
† Methyl vinyl ether, 1221
† Tetrahydrofuran, 1612
† Tetrahydropyran, 1965

See other PEROXIDISABLE COMPOUNDS

DropBooks

ETHOXYETHYNYL ALCOHOLS **$EtOC{\equiv}CCR_2OH$**

1. Arens, J. F., *Adv. Org. Chem.*, 1960, **2**, 126
2. Brandsma, 1971, 12, 78

Vigorous decompositions or violent explosions have been observed on several occasions during careless handling (usually overheating) of ethoxyethynyl alcohols (structures not stated) [1]. The explosions noted when magnesium sulfate was used to dry their ethereal solutions were attributed to the slight acidity of the salt causing exothermic rearrangement of the alcohols to acrylic esters and subsequent explosive reactions (or polymerisation). Glassware used for distillation must be pretreated with ammonia to remove traces of acid [2].

See 4-Ethoxy-2-methyl-3-butyn-2-ol

See other ACETYLENIC COMPOUNDS

EXOTHERMIC DECOMPOSITION REACTIONS

1. Grewer, T., *Proc. 2nd Int. Symp. Loss Prev. Safety Prom. Process Ind.*, III-105–113, 539, Frankfurt, Dechema, 1978
2. Grewer, T., *Chem. Ing. Tech.*, 1979, **51**, 928–933
3. Grewer, T., *Runaway Reactions*, 1981, Paper 2/E, 1–18

Problems in relating chemical structure to the type and course of exothermic decomposition are discussed, with an outline of some general methods useful in following the course of such reactions. Comparative figures for the temperature of onset of decomposition for typical molecular groupings which confer instability are tabulated and the mutual effects of the presence of two such groupings are discussed [1]. The role played by undesired or unexpected reactions in leading to the development of hazards in chemical processing operations is discussed. Typical decomposition energies are assigned to 'unstable' molecular groupings. The results of DTA examination are compared with warm storage tests, and the effects of various substituents and of other substances on the stability of particular compounds are studied [2]. The use of relatively simple tests, either at atmospheric or elevated pressures, to assess the hazards of exothermic decomposition reactions by determining the quasi-adiabatic self-heating curves and induction times are described in detail [3].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

EXOTHERMICITY

Craven, A. D., *Hazards from Pressure*, IChE Symp. Ser. No. 102, Oxford, Pergamon, 1987

A simplified method for near-quantitative estimation of the exothermicity (energy of exothermic decomposition /unit mass) of products or reaction mixtures, which is suitable for a hand-calculator, is presented. It is based on the difference between the total energies of atomization of all the bonds in the starting material(s) and of those in the likely products of decomposition or reaction, rather than on the group contribution methods used with computer programs, which are more accurate but

more complex. Examples are given which show the accuracy of the method to be sufficient for preliminary assessment of potential hazards, together with tabulated values of average bond energies sutable for the purpose.

See also COMPUTATION OF REACTIVE CHEMICAL HAZARDS, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

EXOTHERMIC REACTION MIXTURES IN STEEL MAKING

Babaitsev, I. V. *et al., Chem. Abs.*, 1987, **107**, 138866

Minimum impact energies to initiate the explosion of various exothermic mixtures, used for the continuous casting of steel, were determined. Components used included sodium nitrate, aluminium–iron scale, silicocalcium, ferrosilicon; fluorspar, borax, etc. Hazardous mixtures were defined, and improved safety controls were derived.

EXPLOSIBILITY

1. Lothrop, W. C. *et al., Chem. Rev.*, 1949, **44**, 419–445
2. Tomlinson, W. R. *et al., J. Chem. Educ.*, 1950, **27**, 606–609
3. Coffee, R. D., *J. Chem. Educ.*, 1972, **49**, A343–349; *Chemical Stability*, Chapter 17 in *Safety & Accident Prevention in Chemical Operations*, Fawcett, H. H. & Wood, W. S. (Eds.), New York, Wiley, 2nd edn., 1982
4. Van Dolah, R. W., *Ind. Eng. Chem.*, 1961, **53**(7), 50A –53A
5. Stull, D. R., *Chem. Eng. Progr.*, 1973, **7**, 67–73; reprinted *J. Chem. Educ.*, 1974, **5** 1(1), A21–25
6. Spear, R. J. *et al.*, *Rept. MLR-R-850, AR-003-031*, Richmond (Va.) USNTIS, 1982
7. Chahine, G., *Inform. Chim.* (Paris), 1987, (283), 141–143
8. Melhem, G. A. *et al., Process Safety Progr.*, 1996, **15**(3), 168

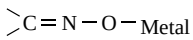
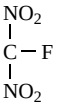
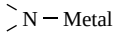
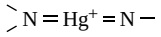
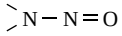
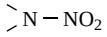
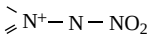
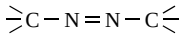
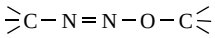
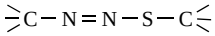
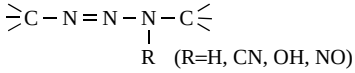
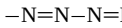
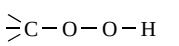
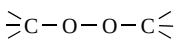
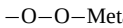
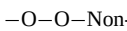
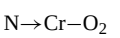
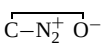
DropBooks

Explosibility may be defined as the tendency of a chemical system (involving one or more compounds) to undergo violent or explosive decomposition under appropriate conditions of reaction or initiation. It is obviously of great practical interest to be able to predict which compound or reaction systems are likely to exhibit explosibility (and the degree exhibited), and much work has been devoted to this end. Early work [1] on the relationship between structure and performance of 176 organic explosives (mainly nitro compounds or nitrate esters) was summarised and extended in general terms to multi-component systems [2]. The contribution of various structural factors (bond-groupings) was discussed in terms of heats of decomposition and oxygen balance of the compound or compounds involved in the system. Materials or systems approaching stoicheiometric composition (zero oxygen balance) are the most powerfully explosive, giving the maximum heat energy release. Bond groupings (see below) known to confer explosibility were classed as ‘plosophores’, and explosibility-enhancing groups as ‘auxoploses’ by analogy with dyestuffs terminology. The latter groups (ether, nitrile or oximino) tend to increase the proportion of nitrogen and/or oxygen in the molecule towards (or past) zero oxygen balance.

Although the semi-empirical approach outlined above is of some value in assessing potential explosibility hazards, much more fundamental work has been done in recent years to institute a more quantitative basis for such assessment. A combination of thermodynamical calculations with laboratory thermal stability and impact-sensitivity determinations has allowed a system to be developed which indicates the relative potential of a given compound or reaction system for sudden energy release, and the relative magnitude of the latter [3]. A similar treatment, specifically for compounds designed or expected to be explosives, was developed earlier [4]. A further computational technique which took account of both thermodynamic and kinetic considerations permitted the development of a system which provides a numerical Reaction Hazard Index (RHI) for each compound, which is a real, rather than a potential, indication of hazard. The RHI's calculated for 80 compounds are in fairly close agreement with the relative hazard values (assessed on the basis or experience) assigned on the NFPA Reactivity Rating scale for these same compounds [5]. In the context of the preparation of highly energetic materials, recent developments in methods of prediction of explosive properties are discussed briefly [6]. Recent information on methods of predicting explosive instability in organic and organometallic compounds is included in a general survey of this topic [7]. It is suggestd that the Calculated Adiabatic Reaction Temperature, CART, the temperature the reaction products would attain under adiabatic containment is generally a better predictor of explosive risk than is the simple heat of reaction since it allows for the variable thermal capacities of the products. It is not too good for organic peroxides. Both techniques depend upon selecting the right decomposition reaction [8].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, COMPUTATION OF REACTIVE CHEMICAL HAZARDS, EXOTHERMIC DECOMPOSITION, OXYGEN BALANCE, THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

BOND GROUPINGS	*as in*	*CLASS ENTRY*
−C=C−		ACETYLENIC COMPOUNDS
−C=C−Metal		METAL ACETYLIDES
−C=C−X		HALOACETYLENE DERIVATIVES DIAZIRINES
$>CN_2$		DIAZO COMPOUNDS
$\geq C-N=O$		NITROSO COMPOUNDS
$\geq C-NO_2$		NITROALKANES, *C*-NITRO and POLYNITROARYL COMPOUNDS
		POLYNITROALKYL COMPOUNDS TRINITROETHYL ORTHOESTERS
$\geq C-O-N=O$		ACYL OR ALKYL NITRITES
$\geq C-O-NO_2$		ACYL OR ALKYL NITRATES

	1,2 EPOXIDES
	METAL FULMINATES or *aci*-NITRO SALTS, OXIMATES
	FLUORODINITROMETHYL COMPOUNDS
	*N*-METAL DERIVATIVES
	POLY(DIMERCURYIMMONIUM SALTS)
	NITROSO COMPOUNDS
	*N*-NITRO COMPOUNDS
	*N*-AZOLIUM NITROIMIDATES
	AZO COMPOUNDS
	ARENEDIAZOATES
	ARENEDIAZO ARYL SULPHIDES
	BIS-ARENEDIAZO OXIDES
	BIS-ARENEDIAZO SULPHIDES
	TRIAZENES
	HIGH-NITROGEN COMPOUNDS TETRAZOLES
	ALKYLHYDROPEROXIDES, PEROXYACIDS
	PEROXIDES (CYCLIC, DIACYL, DIALKYL), PEROXYESTERS
	METAL PEROXIDES, PEROXOACID SALTS
	PEROXOACIDS, PEROXYESTERS
	AMMINECHROMIUM PEROXOCOMPLEXES
	AZIDES (ACYL, HALOGEN, NON-METAL, ORGANIC)
	ARENEDIAZONIUM OXIDES

DropBooks

$\geq C-N_2^+S^-$	DIAZONIUM SULPHIDES AND DERIVATIVES, 'XANTHATES'
$N^+-H\ Z^-$	HYDRAZINIUM SALTS, OXOSALTS OF NITROGENOUS BASES
$-N^+-OH\ Z^-$	HYDROXYLAMINIUM SALTS
$\geq C-N_2^+Z^-$	DIAZONIUM CARBOXYLATES or SALTS
$[N\rightarrow Metal]^+\ Z^-$	AMMINEMETAL OXOSALTS
$Ar-Metal-X$	HALO-ARYLMETALS
$X-Ar-Metal$	HALOARENEMETAL π-COMPLEXES
$N-X$	HALOGEN AZIDES *N*-HALOGEN COMPOUNDS *N*-HALOIMIDES
$-NF_2$	DIFLUOROAMINO COMPOUNDS *N,N,N*-TRIFLUOROALKYLAMIDINES
$N-O-$	N−O COMPOUNDS
$-O-X$	ALKYL PERCHLORATES AMINIUM PERCHLORATES CHLORITE SALTS HALOGEN OXIDES HYPOHALITES PERCHLORYL COMPOUNDS

EXPLOSIONS

Stull, 1977

Fundamental factors which contribute to the occurrence of fire and explosions in chemical processing operations have been collected and reviewed in this 120-page book, which serves as an extremely informative guide to the whole and complex subject, subdivided into 12 chapters. These are: Introduction; Thermochemistry; Kinetochemistry; Ignition; Flames; Dust Explosions; Thermal Explosions; Gas Phase Detonations; Condensed Phase Detonations; Evaluating Reactivity Hazard Potential; Blast Effects, Fragments, Craters; Protection Against Explosions. There are also 3 Appendices, 153 references and a Glossary of Technical Terms.

EXPLOSIVE BOILING

1. Vogel 1957, 4
2. Weston, F. E., *Chem. News*, 1908, 27

The hazards associated with the addition of nucleating agents (charcoal, porous pot, pumice, anti-bumping granules, etc.) to liquids at or above their boiling points have been adequately described [1]. The violent or near-explosive boiling which ensues is enhanced by gases adsorbed onto such solids of high surface area. Incidents involving sudden boiling of salt solutions being concentrated for crystallisation in vacuum desiccators have also been described. The heat liberated by rapid crystallisation probably caused violent local boiling to occur, and the crystallising dishes (soda glass) were fractured [2].

EXPLOSIVE COMBUSTION

1. Lafitte, P. *et al.*, *Hautes Temp., Leurs Util. Phys. Chim.*, 1973, **1**, 1–40
2. Gardner, G., *Chemical Engineer*, 1994, (563), 153.

A comprehensive review includes autoignition of gas mixtures, explosions at low and high temperatures, properties of flames and combustion of metals [1]. A review of explosion suppression techniques for dust, mist or vapour deflagrations, as an alternative to venting industrial plant [2].

EXPLOSIVES

1. Federoff, 1960–1987
2. *Explosives, Propellants and Pyrotechnic Safety Covering Laboratory, Pilot Plant and Production Operations*: Manual AD-272-424, Washington, US Naval Ordnance Laboratory, 1962
3. Kirk-Othmer, 1980, Vol. 9, 561–671
4. Ullmann, 1990, A10, 143
5. Urbanski, 1964–1984, Vols. 1–4.
6. *Explosives* Köhler, J. & Meyer, R., Weinheim, VCH, (4th Edn), 1993

Explosive materials intended as such are outside the scope of this work and many, even of those in widespread use, do not have an entry. Several specialist reference works on them contain much information relevant to their properties and safety practices for unstable materials.

FERROALLOY POWDERS — Fe–Mn, Fe–Si, Fe–Ti

Barbaitsev, I. V. *et al.*, *Chem. Abs.*, 1983, **99**, 161983

Explosion parameters have been measured for ferromanganese, ferrosilicon and ferrotitanium powders in a 1 m^3 chamber. Maximum pressures of 2.8–3.9 bar, at maximum rates of rise of 8.9–21.8 bar/s were determined. Individual entries are:

Ferromanganese, 4389

Ferrosilicon, 4390

Ferrotitanium, 4391

See other ALLOYS

DropBooks

FERTILISER

1. Baccarani, C., *et al.*, *Chem. Abs.*, 1992, **117**, 177392
2. Laing, M., *J. Chem. Educ.*, 1993, **70**(5), 392

Self-sustaining thermal decomposition of NPK fertilisers is apparently possible if crystalline potassium nitrate is present from a exchange reaction of ammonium nitrate [1]. Almost pure fertiliser grades of ammonium nitrate are legally restricted in some countries because of its instability [2].

See Ammonium nitrate

FINELY DIVIDED METALS

1. Manuev, N. V. *et al.*, *Chem. Abs.*, 1979, **90**, 111642
2. Murdock, T. O., *Diss. Abs. Int. B*, 1978, (9), 1291

Requirements for safe storage of powdered Al, Hf, Mg, Ti, Zn and Zr are outlined. Fires are best extinguished with various fluxes, trimethyl boroxine, asbestos fines (!), talc, graphite, sodium chloride, soda ash, lithium chloride or powdered dolomite [1]. Slurries of Al, Cd, Cu, Ge, In, Ni, Pb, Sn or Zn produced by metal atom–solvent cocondensation at −196°C are extremely active chemically [2], and would be pyrophoric on exposure to air.

See Aluminium: Diethyl ether *See other* METAL DUSTS

FIRE

1. *Fire Protection Handbook*, Quincy (Ma.), National Fire Protection Association, 16th edn., 1986
2. Fire Service Abstracts, (quarterly since 1981), Boreham Wood., Fire Research Station
3. Bahme, 1972
4. Meidl, 1972
5. *Fire and Related Properties of Industrial Chemicals*, London, Fire Protection Association, 4th edn., revised 1974
6. *Fire-Hazard Properties of Flammable Liquids, Gases and Volatile Solids*, 325M, Quincy (Ma.), NFPA, 1984
7. *Matrix of Electrical and Fire Hazard Properties and Classification of Chemicals*, AD-A027 181/7GA, Richmond (Va.), USNTIS, 1975
8. *Fire Precautions in Chemical Plant: A Code of Practice*, BS 5908: 1980
9. *DH-HLH-88*, 1988; *NFPA 45*, 1986, Quincy (Ma), National Fire Protection Association

The handbook covers all aspects of fire protection and remedial measures, including those for involvement of chemicals in storage or in process operations [1]. The compilation of references to the scientific literature on fire has been renamed [2] and is now a quarterly publication subdivided and classified as previously. Further aspects, with examples of the special extinguishing problems arising from involvement of reactive chemicals in fires, are detailed [3,4]. The tabulated list of the physical and fire-hazardous properties of some 800 industrially significant chemicals [5] has a US counterpart covering 1300 materials [6]. A matrix relates fire hazardous properties of 226 commercial chemicals to the classification groups of the US National Electrical Code [7]. A UK Code of Practice is applicable to all chemical industry [8], and two recent US fire codes cover electrical installations in hazardous locations, and requirements for chemical-using laboratories, respectively [9].

FIRE EXTINGUISHERS

1. *Fire Safety Data Sheets 6001*–6003, London, Fire Protection Association
2. Hirst, R., *Chem. Engr.*, 1974, 627–628, 636
3. Anon., *Loss Prev. Bull.*, 1978, (022), 107–113
4. Webster, J. M., *Fire Surveyor*, 1984, **13**(2), 5–7
5. Hird, D., *Fire Prev.*, 1987, (202), 20–26

Three illustrated data sheets cover the choice; siting, care and maintenance; and use of portable fire extinguishers [1]. Detailed accounts of modern extinguishing

agents and their use in chemical environments are available [2,3]. Of 3 types of multipurpose hand extinguishers tested comparatively (multipurpose powder, halon, and spray foam), the latter provides higher efficiency for a lower level of skill [4]. In a review of foam applications, a list of flammable liquids which destroy the blanketing effect is given. The most adverse effects are shown by ethylamine and isopropylamine, while several esters, ketones, alcohols and glycols have but slight effects on foam stability [5].

FLAMMABILITY

1. Coward, H. F. *et al., Limits of Flammability of Gases and Vapours*, Bull. 503, Washington, US Bur. Mines, 1952
2. Zabetakis, M. G., *Flammability Characteristics of Combustible Gases and Vapours*, Bull. 627, Washington, US Bur. Mines, 1965
3. Shimy, A. A., *Fire Technol.*, 1970, **6**(2), 135–130
4. Hilado, C. J., *J. Fire Flamm.*, 1975, **6**, 130–139
5. Hilado, C. J., *Fire Technol.*, 1977, **13**(3), 195–198
6. Glikin, M. A. *et al., Chem. Abs.*, 1978, **88**, 39541
7. Mullayanov, F. I. *et al., Chem. Abs.*, 1978, **89**, 91976
8. Ducros, M. *et al., Thermochim. Acta*, 1981, **48**, 351–359
9. Khramov, V. V. *et al., Chem. Abs.*, 1982, **96**, 183907
10. Roberts, P. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, E1–E10, Rugby, IChE, 1983
11. Kishore, K. *et al., J. Haz. Mat.*, 1980, **3**, 349–356
12. High, M. S. *et al., Ind. Eng. Chem. Res.*, 1987, **26**, 1395–1399
13. Mitsui, T. *et al., Chem. Abs.*, 1987, **107**, 182611
14. Hodo, H. *et al., Int. Chem. Eng.*, 1987, **27**(4), 709–715
15. Zetsepin, V. M., *Chem. Abs.*, 1988, **109**, 98069
16. Ducros, M. *et al., J. Haz. Mat.*, 1988, **19**, 33–49
17. Mulzyczuk, J., *Chem. Abs.*, 1989, **110**, 12860
18. Lihou, D., *J. Loss Prevention*, 1993, **6**(4), 266
19. Barfuss, S. *et al., Arch. Combust.*, 1993, **13**(1–2), 33
20. Melhem, G. A., *Process Safety Progr.*, 1997, **16**(4), 203

The hazards associated with flammability characteristics of combustible gases and vapours are excluded from detailed consideration in this Handbook, since the topic is adequately covered in standard reference works on combustion, including the 2 sources of much of the data on flammability limits [1,2].

However, to reinforce the constant need to consider flammability problems in laboratory and plant operations, the flammability (or explosive) limits have been included (where known) for those individual substances with flash points below 25°C. With the few noted exceptions, explosive limits quoted are those at ambient temperature and are expressed as % by volume in air in Appendix 2.

Semi-empirical formulae, based only on molecular structure, have been derived which allow flammability limits to be calculated for hydrocarbons and alcohols. Flash points, autoignition temperatures and boiling points may also be calculated from molecular structure for these classes. Quoted examples indicate the methods

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to be reasonably accurate in most cases [3]. Equations are given for calculating upper and lower flammability limits of 102 organic compounds (hydrocarbons, alcohols, ethers, esters, aldehydes, ketones, epoxides, amines and halides) from structure and stoicheiometry in air [4]. The HC value (Hazardous Concentration, the ratio of the concentration of a substance to its lower flammable limit in the same units) is useful in estimating flammable limits of mixtures of combustible gases [5]. Equations have been derived to calculate the LEL for an organic compound as a function of the number of carbon atoms, the heats of formation of the compound and of an alkane of the same carbon number, state of aggregation, etc., [6], and for petroleum products and their components [7].

The criteria defined by the CHETAH program (*See* COMPUTATION OF HAZARDS) were used to predict lower and upper flammable limits for various organic (C,H,O,N) compounds, results generally being in good agreement with experimental values [8]. A method for predicting upper flammable limits for C_1-C_8 hydrocarbons has been developed [9]. Determination of flammability limits in a spherical container, rather than in the traditional vertical tubes tends to show rather wider values than the tube method for methane to pentane, and for ethylene. It is proposed that these wider limits are more realistic in practice, and especially for purging purposes in significant volumes [10]. The recent concept of relevance in the context of flammability and extinguishment is that of the minimum oxygen content necessary to support combustion. The Oxygen Index is a quantified measure of this, and is becoming of widespread use for non-volatile flammable solids of many types [11].

A group contribution method has been developed to predict upper flammability limits for pure organic compounds. It is applicable to many homologous series which can be constructed from the groups included, and a procedure is given for calculating the confidence limits of the predictions [12]. The use of a microcomputer to estimate flammability limits for organic compounds is described, based on MW and functional groups present. Estimated LELs agreed well with published data, but there was some deviation in UELs [13]. Factors affecting propagation and quenching of flames in cylindrical pipes were investigated experimentally to establish design criteria for flame arresters. Critical velocity to assure flame quenching was below 5 m/s for an open-sided (venting) arrester, or rather higher when the arrester is inside a pipe [14]. Equations relating upper flammability limits to lower limits have been derived for hydrocarbons. From an experimental or calculated lower limit, the upper limit can be predicted with good accuracy [15]. Use of the CHETAH program to determine the flammability of organic oxygen compounds and to estimate their lower flammability limits has been described [16]. A method of calculating lower and upper flammability limits for complex gas mixtures, based on Le Chatelier's law, is described [17]. A procedure for calculating flammable limits of vapour/air mixes under reduced pressure and with nitrogen enrichment, for safe industrial drying operations, is reported [18]. Prediction of flammable limits, for both pure materials and mixtures in air or oxygen, is attainable by way of theoretical flame temperatures. If these are below 1000−1500 C, the mixture should be non-flammable [20]. It is reported that bubbles of air or oxygen in

flammable liquids can be ignited even at pressures too high for the bubble to be within conventional explosive limits 19].

See OXYGEN INDEX (reference 5)

See also OXYGEN ENRICHMENT

FLASH POINTS

1. *Flash Points*, Poole, BDH Ltd., 1962
2. 'Catalogue KL4', Colnbrook, Koch-Light Laboratories, Ltd., 1973
3. *Flash Point Index of Trade Name Liquids*, 325A, Quincy (Ma.), NFPA, 1972
4. *Properties of Flammable Liquids*, 325M, Quincy (Ma.), NFPA, 1969
5. Prugh, R. W., *J. Chem. Educ.*, 1973, **50**, A85–89
6. Shimy, A. A., *Fire Technol.*, 1970, **6**(2), 135–139
7. Thorne, P. F., *Fire Mater.*, 1976, **1**, 134–140
8. Magdanz, H., *Plaste Kautsch.*, 1977, **24**, 774–777
9. Li, C. C. *et al., J. Fire Flamm.*, 1977, **8**, 38–40
10. Tiedtke, K. H., Ger. Offen., 2 723 157, 1978
11. Saborowska-Szpyrkowa, I. *et al., Chem. Abs.*, 1979, **90**, 189290; 1981, **95**, 64598
12. Gmehling, J. *et al., Ind. Eng. Chem. Fundam.*, 1982, **21**, 186–188
13. Shebeko, Yu. N. *et al., Chem. Abs.*, 1983, **98**, 184837
14. Gooding, C. H., *Chem. Eng. (Intern. Ed.)*, 1983, **90**(25), 88
15. Bodinelli, L., *Chem. Eng. News*, 1982, **60**(28), 4
16. MacDermott, P. E., *Chem. Brit.*, 1974, **10**, 228
17. Mitsui, T., *Chem. Abs.*, 1987, **107**, 222429
18. *Flash points of organic and organometallic compounds*, Stevenson, R. M., New York, Elsevier, 1987
19. Bretherick, L., *Chem. Eng. News*, 1988, **66**(50), 2
20. Hasegawa, K. *et al., J. Loss Prev. Process Ind.*, 1991, **4**(3), 176
21. Kohlbrand, H. T., *Plant/Oper. Progr.*, 1991, **10**(1), 52
22. Anon., *Jahresbericht*, 1991, 73

Flash point is defined as the minimum temperature at which a flammable liquid or volatile solid gives off sufficient vapour to form a flammable mixture with air.

There is usually a fair correlation between flash point and probability of involvement in fire if an ignition source is present in the vicinity of the source of the vapour; materials with low flash points being more likely to be involved than those with higher flash points. While no attempt has been made to include in this Handbook details of all known combustible materials, it has been thought worthwhile to include substances with flash points below 25°C, a likely maximum ambient temperature in many laboratories in warm temperate zones. These materials have been included to draw attention to the high probability of fire if such flammable or highly flammable materials are handled with insufficient care to prevent contact with of their vapours with an ignition source (stirrer motor, hot-plate, energy controller, flame, etc.). The figures for flash points quoted in Appendix 2 are closed cup values except where indicated by (o), and most are reproduced by permission of the two Companies concerned. A comprehensive listing of flash points for commercial liquids and formulated mixtures is also available [3,4].

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A method for estimating approximate flash point temperatures based upon the boiling point and molecular structure was published. This involved calculation of the stoicheiometric concentration in air, followed by reference to a nomograph to give the flash point to within 11°C [5]. Many alternative methods of achieving the same ends have now been published, including one for hydrocarbons and alcohols [6], for mixtures of flammable and non-flammable liquids [7], and for partially miscible liquids (when activity coefficients must be known) [8]. Methods based on relative boiling points [9], or using a flame ionisation detector [10] have been described, and equations for use with multicomponent systems [11], or an additive group contribution method [12] are available among others [13,14]. Although chlorinated solvents are sometimes added to hydrocarbon solvents to raise the flash point, addition of inhibitor-containing 1,1,1-trichloroethane to a petroleum solvent actually reduced the flash point. This was attributed to the effect of the inhibitor [15], but this halogenated solvent, which has no flash point, will in fact burn and other haloalkanes have been shown to catalyse combustion.

The commonly accepted fallacy that liquids at temperatures below their flash points cannot give rise to flammable mixtures in air is dispelled with some examples of process operations with solvents at sub-atmospheric pressures. Under such conditions, flammable atmospheres may be generated at temperatures below the flash point. Thus, the real criterion should be whether flammable atmospheres can exist under given process conditions, rather than a flammable liquid being at a temperature below its flash point [16]. The use of a BASIC microcomputer program to calculate the flash points of organic compounds is described, based on the MW and functional groups present, and constants are given for 20 functional groups. Calculated values are satisfactory for monofunctional compounds, but not always for multifunctional compounds [17]. A new 296 page compilation of flash points is available [18]. There are a few halogenated hydrocarbons for which a flash point cannot be determined by standard tests, and these unfortunately are often described as non-flammable, though they will burn if the ignition source is sufficiently intense. Bromomethane, dichloromethane, trichloroethylene and 1,1,1-trichloroethane are compounds of this type [19].

The Japanese have started to measure the temperature corresponding to a composition of the upper explosive limit of a vapour in air under the name: Upper Flash Point. Some examples are given [20].

Liquids can form explosive atmospheres at temperatures below the flash point appropriate to the pressure in question if agitation is sufficient to form a mist. A destructive instance is reported [21].

Explosion of a reactor consequent upon taking a flash point (which refers to air) as indicating safety limits in pure oxygen is reported [22].

FLASH POWDER

1. Partington, 1967, 364
2. Bentzinger, von R. *et al., Praxis Naturwiss., Chem.*, 1987, **36**, 38
3. Young, J. A., *CHAS Notes*, 1991, **IX**(6), 2

Small portions of mixtures of magnesium powder with aluminium powder, with various oxidants (barium peroxide, barium nitrate, potassium chlorate, or even dry

silica powder) were formerly used for flash photography [1]. During a classroom demonstration, several attempts were necessary before a large amount (20 g) of an old sample of flash powder could be ignited, but when ignition eventually occurred, a 20 cm fireball was produced, which caused severe burns [2]. Larger (20 kg) portions of similar mixtures may ignite more easily, and unexpectedly, with serious blast effects [3].

See Barium peroxide: Metals
Potassium chlorate: Metals, 4017
Magnesium: Silicon dioxide, 4690

FLOUR

Bond, 1991, 48

A common fuel for dust explosions, with the distinction of causing the first such event investigated and recorded (in 1795).

See DUST EXPLOSION INCIDENTS

FLUORINATED COMPOUNDS **RF**

See Lithium tetrahydroaluminate: Fluoroamides
Sodium: Fluorinated compounds, or: Halocarbons (reference 6), 4796

FLUORINATED CYCLOPROPENYL METHYL ETHERS

Methanol, or Water

Smart, B. E., *J. Org. Chem.*, 1976, **41**, 2377–2378

There are hazards involved both during the preparation and after isolation of these materials. Addition of sodium methoxide powder to perfluoropropene in diglyme at −60°C led to ignition in some cases, and the products, 1,3,3-trifluoro-2-methoxycyclopropene (very volatile and flammable), or 3,3-difluoro-1,2-dimethoxycyclopropene, react violently with water or methanol, as does 1-chloro-3,3-difluoro-2-methoxycyclopropane.

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The individual compounds are:
1-Chloro-3,3-difluoro-2-methoxycyclopropene, 1411
3,3-Difluoro-1,2-dimethoxycyclopropene, 1866
1,3,3-Trifluoro-2-methoxycyclopropene, 1414

FLUORINATED ORGANOLITHIUM COMPOUNDS

Anon., *Jahresber.*, 1981, 79

An unspecified partially fluorinated unsaturated ether was converted to the lithium salt with methyllithium in ether. A 70 g preparation exploded violently towards

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the end of the preparation, possibly owing to ingress of air down the stirrer guide when vacuum was applied to the flask. The hazardous nature of such compounds is stressed.

See Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide

See other ORGANOLITHIUM REAGENTS

See other METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

FLUORINATED PEROXIDES AND SALTS **$HOC(CF_3)_2OOM$, F_5SOO-**

Anderson, L. R. *et al., J. Fluorine Chem.*, 1976, **7**, 481–500

Five derivatives, including the *O–O* lithium or sodium salts of the hydrogen peroxide adduct of hexafluoroacetone (2-hydroxyhexafluoro-2-propyl hydroperoxide), and their reaction products with acyl halides, are less flammable or explosive than their hydrocarbon analogues, though less stable than the parent hydroperoxides. Relevant entries are:

∗ Pentafluorosulfur peroxyacetate, 0755

∗ Pentafluorosulfur peroxyhypochlorite, : Haloalkenes, 3990

FLUORINATION

1. Grakauskas, V., *J. Org. Chem.*, 1970, **35**, 723; 1969, **34**, 2835
2. Sharts, C. M. *et al., Org. React.*, 1974, **21**, 125–265
3. Brekhovskikh, M. N. *et al., Mater. Res. Bull.*, 1988, **23**, 1417–1421

Safety precautions applicable to direct liquid phase fluorination of aromatic compounds are discussed [1]. Attention is drawn to the hazards attached to the use of many newer fluorinating agents [2]. In a study of fluorination reactions of hafnium and zirconium oxides by the fluoroxidisers xenon difluoride, chlorine trifluoride and bromine trifluoride, reactivity decreased in the order given [3].

For further references, *see* Fluorine

See ∗Pentafluorosulfur peroxyacetate,

See related UNIT PROCESS OR OPERATION INCIDENTS

FLUOROCARBONS **C_nF_{2n+2}**

Oxygen

1. Dawe, B. *et al., Chem. Eng. News*, 1991, **69**(23), 2
2. Taylor, J. E., *ibid.*, **69**(38), 2
3. Larsen, E. R., *ibid.*, l992, **70**(7), 2
4. Christe, K. O., *ibid.*, 1991, **69**(40), 2

A liquid perfluorocarbon was being used as solvent in an oxidation by oxygen under pressure; more energy was released than expected [1]. It is cautioned that fluorocarbons are not inert to oxidation, presumably to carbonyl fluoride. An explosion has been experienced with perfluorotoluene in like circumstances [2]. A correspondent reports that perfluorotoluene is flammable in air, more saturated perfluorocarbons in pure oxygen [3]. Another detailed the combustion performance of polytetrafluoroethylene: 148 kcal/mole; ignition temperature not below 465°C at 7000 psi of oxygen [4], the product is mostly carbonyl fluoride. Other oxidants may also present a risk in extreme circumstances.

See Oxygen: Polymers
Oxygen: Polytetrafluoroethylene, Stainless steel, 4831
Poly(tetrafluoroethylene): Oxygen, 0629

FLUORODINITRO COMPOUNDS $FC(NO_2)_2-$, $FCH_2C(NO_2)_2-$

1. Peters, H. M. *et al., J. Chem. Eng. Data*, 1975, **20**(1), 113–117
2. Snaeberger, D. F., *Rept. UCID-16141*, Lawrence Livermore Lab., Univ. Calif., 1972

Several fluorodinitro compounds of methane (1,1,1-) and ethane (1,2,2-) are described as explosive, sensitive to initiation by impact, shock, friction or other means [1]. Procedures for safe handling of fluorine and explosive fluoronitro compounds are detailed [2].

FLUORODINITROMETHYL COMPOUNDS $F(O_2N)_2C-$

1. Kamlet, M. J. *et al., J. Org. Chem.*, 1968, **33**, 3073
2. Witucki, E. F. *et al., J. Org. Chem.*, 1972, **37**, 152
3. Adolph, H. J., *J. Org. Chem.*, 1972, **37**, 749
4. Gilligan, W. H., *J. Org. Chem.*, 1972, **37**, 3947
5. Coon, C. L. *et al., Synthesis*, 1973, (10), 605–607
6. Gilligan, W. H. *et al., J. Chem. Eng. Data*, 1982, **27**, 94–99

Several of this group are explosives of moderate to considerable sensitivity to impact or friction and need careful handling. Fluorodinitromethane and fluorodinitroethanol are also vesicant [1]–[4]. 1-Fluoro-1,1-dinitro derivatives of ethane, butane, 2-butene and 2-phenylethane are explosive [5]. Among the preparations of a series of energetic and explosive compounds, that of *N,N,N′,N′*-tetrakis(2-fluoro-2,2-dinitroethyl)oxamide is especially hazardous, as it involves heating an undiluted explosive to a high temperature [6].

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Individually indexed compounds are:
Bis(2-fluoro-2,2-dinitroethoxy)dimethylsilane, 2421
Bis(2-fluoro-2,2-dinitroethyl)amine, 1459
2,2-Dinitro-2-fluoroethoxycarbonyl chloride, 1072
1-Fluoro-1,1-dinitrobutane, 1562
4-Fluoro-4,4-dinitrobutene, 1458
1-Fluoro-1,1-dinitroethane, 0748
∗ 2(?)-Fluoro-1,1-dinitroethane, 0749
2-Fluoro-2,2-dinitroethanol, 0750
2-Fluoro-2,2-dinitroethylamine, 0800
Fluorodinitromethane, 0374
Fluorodinitromethyl azide, 0341
1-Fluoro-1,1-dinitro-2-phenylethane, 2934

See also ENERGETIC COMPOUNDS

FOAM BLANKETING FOR SPILL CONTROL

1. DiMaio, L. R. *et al., Plant/Oper. Progr.*, 1988, **7**, 195–198
2. Norman, E. C., *Vapour suppression by aqueous foams*, Chapter 2 in *Hazardous and toxic materials*, Fawcett, H. H. (ed.), New York, Wiley, 2nd edn., 1988

The use of aqueous foams to control fume or vapour release from reactive chemicals is discussed. An acid-resistant foam NF2 controlled fume emission from 35% and 65% oleum, and from titanium tetrachloride, but was not effective for sulfur trioxide and chlorosulfuric acid. An alcohol-resistant foam NF1 suppressed ammonia vapour emission by 80%, and Universal fire foam reduced evaporation of ethylene oxide, vinyl chloride and methanethiol, and reduced vapour emission of 1,3-butadiene by 60%. Safety aspects of foam blanketing are discussed [1]. Equipment and application techniques are covered in some detail [2].

FOAM RUBBER

1. Woolley, W. D. *et al., BRE CP 36/75*, Garston, Building Res. Est., 1975
2. Smith, E. E., *Consum. Prod. Flammability*, 1975, **2**, 589–69

A fire involving foam rubber mattresses in a storeroom led to an unexpected and serious explosion. Subsequent investigation showed that an explosion risk may exist when the flammable smoke and vapour from smouldering of large amounts of foam rubber are confined in an enclosed space. Suitable strict precautions are recommended [1]. Methods of quantitatively evaluating potential fire hazards from release rates of heat, smoke and toxic gases from heated foam rubber and plastics materials were developed, and their application to real situations discussed [2].

Oxygen

See Oxygen (Gas): Polymers

FREEZE DRYING

See Sodium azide: Heavy metals (references 4,5)

FRICTIONAL IGNITION OF GASES AND VAPOURS

1. Powell, F., *Ind. Eng. Chem.*, 1969, **61**(12), 29
2. Desy, D. H. *et al., Rept. RI 8005*, Washington, US Bur. Mines, 1975
3. Uchida, S. *et al., Chem. Abs.*, 1984, **101**, 154290
4. van Laar, G. F. M., *EuropEx Newsl.*, 1986, (2), 9
5. Ihara, H. *et al., Chem. Abs.*, 1987, **107**, 80558
6. Krasnayanskii, M. M. *et al., Chem. Abs.*, 1987, **107**, 204305
7. Bartknecht, J., *Plant/Oper. Progr.*, 1988, **7**(2), 114–121.

The ignition of flammable gases and vapours by sparks from friction or impact was reviewed [1]. Ignition of methane by frictional impact of aluminium alloys and rusted steel has been investigated [2]. The effect of presence of beryllium in light alloys on the ignition of methane by sparks derived from their impact with rusted or corroded steel has been studied in a mining context [3]. Recent findings

on initiation of gases by mechanically derived sparks are discussed, including relationships between ignition sensitivity and minimum ignition temperatures and energies [4]. Ignition of methane by sparks produced by continuous contact of various metals with a rotating disc of the same or another metal has been studied [5]. From a study of a wide range of flammable organic vapours and gases by frictional sparks, it was concluded that only mixtures containing acetylene, carbon disulfide, carbon monoxide, hydrogen or methane could be so ignited. However, this conclusion is stated to be irrelevant if the temperature of the frictional surfaces exceeds the autoignition temperatures of the mixtures, or reaches 50–70°C [6]. The ignition capability of mechanically generated sparks or hot surfaces for gas and dust–air mixtures have been studied experimentally. A previous analysis of 357 industrial dust explosions had concluded that 30% were caused by mechanical sparks, and 5% by hot surfaces, but the results of the present work show that the converse is likely to be true [7].

See FRICTIONAL INITIATION OF DUST CLOUDS
See IGNITION SOURCES, THERMITE REACTIONS

FRICTIONAL INITIATION INCIDENTS

1. Cartwright, R. V., *Chem. Eng. News*, 1983, **61**(6), 4
2. Négyesi, G., *Process Safety Progress*, 1996, **15**(1), 42
3. Négyesi, G., *Process Safety Progress*, 1997, **16**(4), 237

Following the explosion of a perchlorate salt during filtration on a sintered funnel which caused severe injuries, the advantages of using plastic sintered funnels were stressed. Frictional heating will be much less on plastic sinters, and if explosive decomposition is initiated on a plastic funnel, fragmentation and resulting injuries should be much less with, for example, high-density polythene. (If the use of perchlorate salts cannot be avoided, fully appropriate measures for personal protection in addition to the use of plastic sinters seem essential [1].) Many non-explosive organic compounds, usually containing N or S heteroatoms, show decomposition, charring or sparks when subjected to friction or, less often, impact tests. This may be important as a souce of ignition during grinding. Of 167 compounds tested, mostly pharmaceuticals and intermediates, 36 (listed) showed friction sensitivity. Testing of suspect compounds prior to industrial milling is suggested, with inerting or explosion protection measures for those proving positive [2]. Investigation of friction sensitivity of various pharmaceutical intermediates suggested that nitrogen-heterocycle carbothionamides may be sensitive to frictional ignition, apparently because of decomposition to give carbon disulphide and hydrogen sulphide, which have very low auto-ignition temperatures [3]. Other instances of frictional initiation are indexed under:

Barium: Halocarbons, 0200
Barium peroxide, 0216
1,2-Bis(azidocarbonyl)cyclopropane, 1835
∗ Calcium hypochlorite, 3924
Chromium trioxide: Potassium hexacyanoferrate(3–), 4242
Diazidodimethylsilane, 0918

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Diazoacetonitrile, 0675
∗ Dimercury dicyanide oxide, 0983
Dimethylketene, 1518
Dysprosium perchlorate, 4131
Erbium perchlorate, 4132
Hexaamminechromium(III) perchlorate, 4129
† Phosphorus, 4874
Potassium chlorate: Metal phosphinates, 4017
Potassium perchlorate, 4018
Sodium 5-azidotetrazolide, 0551
Sodium chlorate : Paper, Static electricity, 4039
Sodium chlorate: Wood, 4039
Succinoyl diazide, 1438
Tetrakis(chloroethynyl)silane, 2879
Thianthrenium perchlorate, 3455
Triferrocenylcyclopropenium perchlorate, 3885
See other IGNITION SOURCES

FRICTIONAL INITIATION OF DUST CLOUDS

1. Pederson, G. H. *et al., Arch. Combust.*, 1987, **7**(1−2), 59−83
2. Dahn, C. J. *et al., ASTM Spec. Tech. Publ. 958,* (Ind. Dust Explos.), 1987, 324−332

At net impact energies below 20 J (approach velocities of 10−25 m/s), the heat generated by single impacts between various steels, between steel and rusty steel or concrete was insufficient to ignite dust clouds of corn starch, grain, feedstuffs or flour, even if dry. Dry dusts of titanium or zirconium may ignite, but not if 10% moisture is present in the cloud. Turbulence from a moving object in a dust cloud reduced the ignitability in the vicinity of the object. Impacts against a coarse surface (gravel) produced more sparking than against a smooth (cement-covered concrete) surface [1]. Six alloys, 2 of aluminium, a mild steel and 3 stainless were assessed for their ability to produce frictional sparks and to ignite dust clouds of various propellants and corn starch. The aluminium alloys showed the least hazard potential, and the ferrous alloys a greater tendency to cause ignition, particularly above frictional speeds of 9.2 m/s, and especially for long contact times [2].
See also FRICTIONAL IGNITION OF GASES AND VAPOURS

FRICTION DUST

Unpublished information, 1979

This is used in manufacture of brake linings and is a polymer based on cashew nutshell liquid admixed with formaldehyde or furfuraldehyde and other ingredients. The polymerised resin mixture is cast into 8 cm thick slabs and then ground finely to produce the friction dust. Several fires have been experienced during bulk storage of the dust, attributed to autoxidation of the still partially unsaturated resin compound. Previously, linseed oil was used in place of the nutshell liquid, but fires were then more frequent.

FULLER'S EARTH

Turpentine
See TURPENTINE: diatomaceous earth

FULMINATING GOLD

Ephraim, 1939, 462–463
This appears not to be one specific compound or mixture, but is of variable composition, depending on the method of preparation. Prepared from gold chloride and aqueous ammonia, the explosive precipitate is largely $(ClAuNH_2)_2NH$, but on washing with ammonia hydrolysis to the more explosive $(HOAuNH_2)_2NH$ occurs, and the equilibrium is reversed by washing with chloride.
See Gold(III) chloride (and the entries following).

FULMINATING METALS

1. Tan, K. G., *Can. Inst. Metals Bull.*, 1987, **80**(903), 96–97
2. Bretherick, L., *Chem. Haz. Ind.*, 1988, (8), item 1595
3. Wilhelm, S. M., *Plant/Oper. Progr.*, 1991, **10**(4), 192

The fallacy that the 'fulminating silver' and 'fulminating gold' produced by reaction of ammonia with silver or gold salts are silver fulminate or gold fulminate is perpetuated in a recent publication [1]. In fact, 'fulminating silver' is largely silver nitride, Ag_3N, and 'fulminating gold', while of less certain constitution, contains several Au–N bonds. In contrast, the true fulminates, salts of hydrogen cyanide *N*-oxide, contain C–metal bonds [2].

Although the description 'fulminating' is not used and thus confusion with the fulminate not caused, mercury also forms explosive compounds of similar nature. The nitride (*ibid.*) is the most common and can be formed from the metal and ammonia in some circumstances, causing accidents where mercury manometers are used with ammonia. Halo-hydroxy- and oxy-nitrides can also be involved [3].
See METAL FULMINATES, GOLD COMPOUNDS, *N*-METAL DERIVATIVES, PRECIOUS METAL DERIVATIVES, SILVER COMPOUNDS

DropBooks

FULMINATING SILVER

Ephraim, 1939, 462
Fulminating silver is the most violently explosive compound among the nitrogen derivatives of the noble metals. Formed from action of ammonia on silver oxide, or on addition of potassium hydroxide to an ammoniacal solution of a silver salt, it is a black powder which explodes violently in the liquid in which it is formed if the slightest stirring is used. It probably contains amminesilver hydroxides, $[Ag(NH_3)_x]OH$.
See Silver chloride: Ammonia
Silver nitrate: Ammonia (4 items), 0022

FUMES

1. Smith-Hansen, L. *et al., J. Loss Prevention*, 1993, **6**(4), 227; *ibid.*, 1995, **8**(2), 127
2. Christiansen, V., *J. Loss Prevention*, 1994, **7**(1), 39
3. Smith-Hansen, L., *Risoe Natl. Lab., [Rep] Risoe-R*, 1994; *Chem. Abs.*, 1995, **122**, 247076u
4. Smith-Hansen, L. *et al., Risoe Natl. Lab., [Rep] Risoe-R*, 1995; *Chem. Abs.*, 1996, **124**, 65180g

Readers have indicated that they regard information on toxic fumes emitted in fires as important. This is not a simple subject and little is definitely known. Other reference works are packed with improbable products of 'heating to decomposition' (which is seldom distinguished from combustion). These appear to be the product of simplistic extrapolations from the empirical formulae. They also commonly list species which can have no existence under any conditions the human frame can tolerate, although they may, indeed, be present at 1000°C. What little experimental study has been reported indicates that in reality, as one would expect, the off-gases depend greatly on the fire conditions. Some Scandinavian studies have looked at pesticides, which contain an unusual wealth of hetero-atoms [1,2,3,4]. There are always fumes of water, carbon monoxide and carbon dioxide. Nitrogen may appear as the element, as ammonia, as hydrogen cyanide or as NOx; sulphur as the element, as hydrogen sulphide and as sulphur dioxide. Phosphorus will emerge mostly as the pentoxide, (which will have picked up water before it gets near the lungs) and may possibly sometimes appear as phosphine. Chlorine usually appears as hydrogen chloride, but partially as the element and sometimes as phosgene. Bromine and iodine are more likely to appear as the element. Most of these materials seldom reach the levels of a 30 minute LC_{50}.

Genuine acute dangers appear to be heat (the lungs cannot take air much above 60°C), oxygen depletion and carbon monoxide. These are found in all fires, even those involving no "chemicals" as the environmentalist considers them. The obstruction to the lungs' function caused by deposition of solid carbon particles (soot) is also not chemical but none the less deleterious for that. Sulphur dioxide and hydrogen chloride (both readily detected irritants) may reach dangerous levels; hydrogen cyanide probably never does (except under conditions where CO is the greater danger) and nitrogen oxides only when the NO bond was already present in the starting material. Some NOx, the product of heating air, is always formed by hot fires anyway. Certain materials, such as fats, may produce irritant, if not actually toxic, fumes of propenal but poisonous organic fumes seem rare. However, pyrolysis is an excellent way of producing high energy species such as may induce chronic effects by interaction with nucleic acids, whether the starting material be tobacco, cannabis, dried banana-skin or whatever. It is not healthy to inhale more smoke than can be helped.

Readers are warned that the literature includes some incident reports originating from the emergency services which are undoubtedly in error. An example is the claimed production of hydrogen cyanide by fuels containing no nitrogen, but much chlorine (the ordinary gas detection tubes for cyanide actually generate and then

measure hydrogen chloride; for which they have very limited absorption capacity in the pre-layer).

FURAZAN *N*-OXIDES

1. Barnes, J. F. *et al.*, *J. Chem. Soc., Perkin Trans.*, 1983, 294–295
2. Barnes, J. F. *et al.*, *J. Chem. Soc., Chem. Comm.*, 1978, 113–114
3. Naixing, W. *et al.*, *Propellants, Explos., Pyrotech.*, 1994, **19**(3), 145

Low MW strained-ring furazan *N*-oxides (furoxans) and some of their precursors are highly energetic compounds and should be handled carefully with due caution [1], and preferably in solution [2]. Benzofuroxans are reviewed, especially in relation to their explosive properties, which may be superior to corresponding nitrocompounds in energy, speed of detonation and bulk density [3].

Individually indexed compounds are:

4-(2′-Ammonio-2′-carboxyethylthio)-5,7-dinitro-4,5-dihydrobenzofurazanide *N*-oxide, 3146
Benzotri(furazan *N*-oxide), 2631
3(3-Cyano-1,2,4-oxadiazol-5-yl)-4-cyanofurazan 2- (or 5-) oxide, 2630
4,5-Cyclopentanofurazan-*N*-oxide, 1871
Dicyanofurazan *N*-oxide, 1804
4,6-Dinitrobenzofurazan *N*-oxide, 2089
∗ 3-Ethyl-4-hydroxy-1,2,5-oxadiazole, 1504
4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2357
Potassium 4-hydroxyamino-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2176
Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2114
Potassium 3-methylfurazan-4-carboxylate 2-oxide, 1415
4a,5,7a,8-Tetrahydro-4,8-methano-4*H*-indeno[5,6-*c*]-1,2,5-oxadiazole 1- and 3-oxide, 3282

See other *N*-OXIDES

DropBooks

GAS CYLINDERS

1. *The Safe Filling, Handling, Storage and Distribution of Gases in Transportable Containers*, Code of Practice CP9, London, Brit. Comp. Gases Assoc., 1982
2. *Properties of Gases*, Wall Chart 57012, Poole, BDH Chemicals Ltd., 3rd edn., 1981
3. Braker, W. *et al.*, *Matheson Gas Data Book*, E. Rutherford (NJ), Matheson Gas Products, 6th edn., 1981
4. *Guide to Safe Handling of Compressed Gases*, Lyndhurst (NJ), Matheson, 1982
5. *Handbook of compressed gases*, Compressed Gas Association Inc., New York, Van Nostrand-Reinhold, 2nd ed., 1981

The *Code of Practice* covers UK legislation, containers, identification and marking, valves, handling and storage, transportation, emergency procedures and personnel training. Data sheets for 114 gases are included [1]. An inexpensive wall chart summarises the important properties of 116 gases and volatile liquids [2]. The

Gas Data Book gives comprehensive details of handling techniques and cylinder equipment necessary for 120 gases [3], and the newer guide covers the design of gas systems, premises, cylinder handling and storage, and air-monitoring techniques for a range of gases [4]. Another volume covers all aspects of handling gases in gas, liquid and solid states [5].

GAS EVOLUTION INCIDENTS

1. Lubernau, J. O., *Health Phys.*, 1986, **51**(1), 147
2. Lambert, P. G. *et al.*, *Chem. & Ind.*, 1987, 490–491
3. Carson, P. J. *et al.*, *Loss Prev. Bull.*, 1992, (102), 15
4. Lambert, P. G. *et al.*, *Chem. Eng. Progress*, 1992, **88**(10), 53

Several incidents of pressure build-up in sealed containers of solutions of radioactive materials are noted for the period 1906–1985. The cause is radiolysis of the solvent, usually water, with evolution of hydrogen [1]. A method for evaluating gas evolution hazards in batch processing has been described. Based upon the use of a corrosion-resistant thermal mass flowmeter in conjunction with normal laboratory glassware, the electrical output can be fed either to a recorder/integrator, or to a data-logger/computer system. To exemplify the method, the rates of evolution of hydrogen chloride during the addition of carbon tetrachloride to a cold mixture of benzene and aluminium chloride (to form trityl chloride) are shown diagrammatically [2]. A list of combinations which may evolve toxic gases is given [3].

Although gas evolution is usually endothermic in open systems, and seldom a problem on laboratory scale, industrial batch reactors combine relatively far smaller vents with lower rupture pressures. This can give dangers with even endothermic evolutions. Exothermic gas evolving reactions readily become uncontrollable. A further hazard is nucleation and heating of saturated and supersaturated gas solutions when crystallisation of products occurs; this is the cause of many reactions jumping from flasks even in the lab. Details of combined calorimetric and gas flow safety-evaluation procedures are given [4]. A danger unremarked by the authors, but present in one of several examples, is autocatalysis of a slow step of the reaction by a non-gaseous product.

Elsewhere in the text, a number of incidents have involved evolution of gas(es) arising from slow decomposition or hydrolysis in storage, progressive thermal decomposition, or from other miscellaneous reactions or processing faults. Individual incidents may be found under:

Aluminium chloride, : Water, 0062
Aluminium hydride, : Carbon dioxide, or Sodium hydrogen carbonate, 0070
Aluminium phosphide, : Mineral acids, 0083
Americium trichloride, 0090
2-Ammoniothiazole nitrate, 1194
Argon, : Liquid nitrogen, 0091
Azidoiodoiodonium hexafluoroantimonate, 4361
Benzenesulfinyl chloride, 2234
Benzenesulfonyl chloride, 2235

Benzyl bromide, : Molecular sieve, 2735
Benzyl chloride, : Catalytic impurities, 2738
1,2-Bis(chloromethyl)benzene, 2946
Bis(2-cyanoethyl)amine, 2397
Bis(trimethylsilyl) peroxomonosulfate, 2602
Borane–tetrahydrofuran, 0138
Butylmagnesium chloride, 1641
Calcium acetylide, : Methanol, 0585
Calcium chloride, 3923
Cerium, : Water, 3961
Chlorine, : Chlorinated pyridine, Iron powder, 4047
Chlorine, : Dichloro(methyl)arsine, 4047
∗ 2-Chloro-*N*-hydroxyacetamidine, 0849
∗ 2-Chloro-*N*-(2-hydroxyethyl)aniline, 2975
2-Chloromethylthiophene, 1842
Chlorosulfuric acid, : Hydrocarbons, 3997
Chlorosulfuric acid, : Sulfuric acid, 3997
Chromic acid, 4229
Chromium(II) chloride, 4052
Cyclohexanone oxime, 2452
1,4-Dicyano-2-butene, 2311
Diethyl dicarbonate, 2444
Diethyl sulfate, : Iron, Water, 1710
(Difluoroamino)difluoroacetonitrile, : Hydrazine, 0630
Difluoroammonium hexafluoroarsenate, 0098
1,1-Difluorourea, 0398
Dihydroxymaleic acid, 1447
† Diketene, : Acids, or Bases, or Sodium acetate, 1441
N,N-Dimethylacetamide, 1656
Dimethylmethyleneoxosulfanenickel(0) diethylene complex, 2856
† Dimethyl sulfoxide, : Sodium hydride, 0921
∗ 1,3-Dioxol-4-en-2-one, 1087
Disulfur dichloride, 4114
† Ethylene oxide, : Polyhydric alcohol, Propylene oxide, 0829
Ethylmagnesium bromide, : Water, 0847
Ethyl oxalyl chloride, 1456
N-Ethyl-*N*-propylcarbamoyl chloride, 2468
† Formaldehyde, : Magnesium carbonate hydroxide, 0416
Formamide, : Iodine, Pyridine, Sulfur trioxide, 0453
Formic acid, 0418
Formic acid, : Palladium–carbon catalyst, 0418
Formic acid, : Phosphorus pentaoxide, 0418
Furan-2-amidoxime, 1872
Hydrogen chloride, : Chlorine, Dinitroanilines, 3993
Hydrogen chloride, : Sulfuric acid, 3993
Hydrogen peroxide, : Catalyst (unspecified), 4477

DropBooks

Hydrogen peroxide, : Copper(II) chloride, 4477
Hydrogen peroxide, : Iron(III) chloride, Hydrocarbons, 4477
Hydrogen peroxide, : Methanol, Copper sulfate, Cyanide residues, 4477
Hydrogen peroxide, : Polymer residues, 4477
Hydrogen peroxide, : 2-Propanol, 4477
Iron, : Water, 4388
Lithium, : 1,2-Diaminoethane, Tetralin, 4680
Lithium tetrahydroaluminate, : Fluoroamides, 0075
Lithium tetrahydroaluminate, : Water, 0075
Magnesium, : Barium carbonate, Water, 4690
Maleic anhydride, : Bases, or Cations, 1404
Mercaptoacetonitrile, 0767
† Methanol, : Hydrogen, Raney nickel catalyst, 0484
Methoxyacetyl chloride, 1165
4-Methoxy-3-nitrobenzoyl chloride, 2916
† Methyl formate, : Methanol, Sodium methoxide, 0834
3-Methyl-2-penten-4-yn-1-ol, 2384
Nitric acid, 4436
Nitric acid, : Acrylonitrile–methacrylate copolymer, 4436
Nitric acid, : Alcohols, 4436
Nitric acid, : 1,4-Bis(methoxymethyl)2,3,5,6-tetramethylbenzene, 4436
Nitric acid, : Formaldehyde, 4436
Nitric acid, : Formic acid, 4436
Nitric acid, : Organic materials, 4436
Nitric acid, : Sulfur halides, 4436
Nitrobenzene, : Tin(IV) chloride, 2262
2-Nitrobenzoyl chloride, 2653
2-Nitrobenzyl bromide, 2710
Orthophosphoric acid, : Chlorides, Stainless steel, 4505
Oxalic acid, : Urea, 0725
Peroxyacetic acid, : Metal chlorides, 0837
Phosphorus tribromide, : Phenylpropanol, 0293
Phosphorus trichloride, : Water, 4153
Phosphoryl chloride, : Water, 4149
Potassium bromate, : Aluminium, Dinitrotoluene, 0255
Pyrimidine-2,4,5,6-(1*H*,3*H*)-tetrone, 1398
Pyruvic acid, 1150
Sodium carbonate, 0552
Sodium chlorate, : or Non-metals, or Sulfides, 4039
Sodium dihydrobis(2-methoxyethoxy)aluminate, 2575
Sodium hydride, : Water, 4444
Sodium hydrogen carbonate, : Carbon, Water, 0390
Sodium hypochlorite, : Sodium ethylenediaminetetracetate, Sodium hydroxide, 4037
Sodium tetrahydroborate, 0147
Sodium tetrahydroborate, : Dimethyl formamide, 0147

Sodium triammine, 4581
Sulfinyl bromide, 0274
Sulfinyl chloride, : Dimethylformamide, 4096
Sulfinyl chloride, : Tetrahydrofuran, 4096
† Sulfur, : Limonene, 4897
Terephthaloyl chloride, 2889
1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, Solvent, 2079
Tetrachloroethylene carbonate, : Tributylamine, 1042
Tetrachlorosilane, : Ethanol, Water, 4173
Titanium, : Water, 4919
2-Toluenediazonium bromide, 2736
Trichloroacetaldehyde oxime, 0698
Trichloroperoxyacetic acid, 0659
Trifluoromethanesulfonic acid, : Acyl chlorides, Aromatic hydrocarbons, 0375
Trimethylsulfonium chloride, 1303
Trimethylsulfoxonium bromide, 1299
Uronium nitrate, 0494

SUGARS
ALKYL NITRATES: lewis acids
CYANIDES: hypochlorites
DEVARDA'S ALLOY
DIAZONIUM TETRAHALOBORATES
ISOXAZOLES
NITROBENZALDEHYDES
NITROBENZYL COMPOUNDS
PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

DropBooks

GAS HANDLING

1. O'Hanlon, J. F. *et al., J. Vac. Sci. Technol. A*, 1988, **6**(3, part 1), 1226–1254
2. *Photovoltaic safety*, Proc. Amer. Inst. Phys. Conf., 1988, 166

The American Vacuum Society's recommended procedures for handling hazardous gases include consideration of pump types, pump fluids, system design, effluent control, and storage of gases used for etching and deposition work. Examples of processes discussed in detail are aluminium plasma etching; silicon nitride, tungsten silicide, boron phosphosilicate-glass, silicon and gallium arsenide deposition; and ion implantation [1]. The conference dealt with various aspects of safety in gas handling systems in photovoltaic production processes, including a practical evaluation of wet gas-scrubbing systems, and a review of controlled combustion or oxidation of waste process gas streams. Gases discussed include arsine, diborane, disilane, hydrogen, hydrogen selenide, hydrogen telluride, phosphine, silane, trimethylaluminium and trimethylgallium [2].

See also CHEMICAL VAPOUR DEPOSITION

GEOMETRY OF VESSELS AND PIPEWORK

1. Phylaktou, H. *et al., J. Loss Prevention*, 1993, **6**(1), 15 & 21
2. Chatrathi, K. *et al., Process Safety Progr.*, 1996, **15**(4), 237
3. Singh, *Process Safety Environ. Protect.*, 1994, **72**(B4), 220

The geometry of a detonable or deflagrating charge has a strong influence upon its performance. Pressure rise on ignition of gas/air mixtures in pipework was studied. In general, departures from the straight and narrow accelerated pressure rise and, presumably, transition to detonation [1]. A study of deflagration to detonation transition in pipes, for gas/air and dust mixtures has subsequently been published [2]. Gas explosions in interconnected vessels generate much higher pressures in the second, due to 'pressure piling'. A mathematical technique for prediction of hazard is given [3].

See also VAPOUR CLOUD EXPLOSIONS, DUST EXPLOSION INCIDENTS

GLASS INCIDENTS

1. Craig, T., *New Scientist*, 1995, **145**(1968), 33

Toughened glass used in fume cupboard windows can occasionally shatter explosively when edge defects are present. Although a physical hazard, it is possible to imagine it triggered by a small chemical explosion, which could even amplify the hazards of flying fragments. Application of polyester film to the outside of such windows is recommended [1].

There are several incidents in the text where glass has been involved as a direct cause, either because of its chemical properties (alkalinity, corrosive attack), or its physical properties (actinic transparency, or mechanical limitations under stress). Some of these incidents may be found under the entries:

Acrylic acid, : Initiator, Water, 1148
Aluminium chloride, : Water, 0062
Barium peroxide, : Propane, 0216
1,3-Benzodithiolium perchlorate, 2677
1,1-Bis(fluorooxy)tetrafluoroethane, 0641
Borane–tetrahydrofuran, 0138
Boron tribromide, : Water, 0122
Bromine, : Aluminium, Dichloromethane, 0261
Bromine, : Tungsten, Tungsten trioxide, 0261
† 1,3-Butadiene, 1480
Calcium oxide, : Water, 3937
Chlorine trifluoride, : Refractory materials, 3981
Chromium trioxide, : Acetic acid, 4242
Copper(II) oxide, : Boron, 4281
Diazoacetonitrile, 0675
Dihydroxymaleic acid, 1447
Ethyl azide, 0872
Ethylmagnesium bromide, : Water, 0847
Formic acid, 4436
† Hydrogen cyanide, 0380

Hydrogen hexafluorophosphate, : Borosilicate glass, 4360
Hydrogen peroxide, : Diethyl ether, 4477
Imidazoline-2,4-dithione, 1141
Lithium nitride, : Silicon tetrafluoride, 4688
Magnesium, : Metal oxides, 4690
Manganese trifluoride, 4335
† Methyl acrylate, 1531
Nitric acid, : Glassware, 4436
Oxalic acid, : Urea, 0725
† Pentaborane(9), : Pentacarbonyliron, Pyrex glass, 0188
† Pentaborane(9), : Reactive solvents, 0188
Potassium hydroxide, : Glass, 4428
Potassium–sodium alloy, : Fluoropolymers, 4646
† Propene, : Lithium nitrate, Sulfur dioxide, 1198
Propiolaldehyde, 1085
Silicon dioxide, : Hydrochloric acid, 4839
Sodium sulfide, : Glass, 4811
Sodium tetrahydroborate, 0147
Succinic anhydride, : Sodium hydroxide, 1443
Sulfuric acid, : Hydrofluoric acid, 4479
Trifluoromethyl hypofluorite, : Lithium, 0353
2,4,6-Trimethylpyrilium perchlorate, 2992
Trimethylsulfonium chloride, 1303
Trimethylsulfoxonium bromide, 1299
Urea hydrogen peroxidate, 0476

DropBooks

GOLD CATALYSTS

Cusumano, J. A., *Nature*, 1974, **247**, 456
Supported metal catalysts containing gold should never be prepared by impregnation of a support with solutions containing both gold and ammonia. Dried catalysts so prepared contain extremely sensitive gold–nitrogen compounds which may explode at a light touch.
See FULMINATING GOLD, GOLD COMPOUNDS

GOLD COMPOUNDS

Many gold compounds exhibit a tendency to decompose violently with separation of the metal. Individually indexed compounds are:
Bis(dihydroxygold)imide, 0114
Chloromercuriodiphenylgold, 3473
Cyclopentadienylgold(I), 1839
∗ 1,2-Diaminoethanebis(trimethylgold), 3105
Diethylgold bromide, 1672
Digold(I) ketenide, 0574
Dimethylgold selenocyanate, 1200

Gold(I) acetylide, 0573
Gold(III) chloride, 0111
Gold(I) cyanide, 0308
Gold(III) hydroxide–ammonia, 0112
Gold(I) nitride–ammonia, 0117
Gold(III) nitride trihydrate, 0118
Gold(III) oxide, 0115
Gold(III) sulfide, 0116
Phenylgold, 2221
Sodium triazidoaurate(?), 0113
Tetracyanooctaethyltetragold, 3814
∗ Tetramethylbis(trimethysilanoxy)digold, 3382
Tetramethyldigold diazide, 1739
Triethylphosphinegold nitrate, 2558

See also PLATINUM COMPOUNDS, SILVER COMPOUNDS

GRAPHITE OXIDE

Boehm, H. P. *et al., Z. Anorg. Chem.*, 1965, **335**, 74–79

The oxide (an intercalated laminar material) is thermally unstable and on rapid heating it will deflagrate at a temperature dependent on the method of preparation. This temperature is lowered by the presence of impurities, and dried samples of iron(III) chloride-impregnated oxide explode on heating.

See related NON-METAL OXIDES

GRAVEL

Forell, B. *et al., Müll. Abfall*, 1998, **30**(5), 327

Falling gravel is found to be an especial risk of ignition in boreholes containing flammable atmospheres. Flint, and some other forms of silica, are, of course, mechanical igniters of some antiquity. This observation brings into question use of gravel as a surface covering near where spills may be expected in chemical plants.

GRIGNARD REAGENTS **RMgX, ArMgX**

1. Kharasch and Reinmuth, 1954
2. Bondarenko, V. G. *et al., Chem. Abs.*, 1975, **82**, 89690
3. Brogli, F. *et al., Runaway Reactions*, Paper 3/M, 4, 7, Rugby, IChE, 1981
4. *See entry* SELF-ACCELERATING REACTIONS
5. Eckert, T. S., *J. Chem. Educ.*, 1987, **64**(2), 179
6. Sharkey, J. J. *et al. J. Loss Prevention*, 1994, **7**(5), 413.

Preparation of Grignard reagents is frequently beset by practical difficulties in establishing the reaction (i.e. is usually subject to an induction period). Improved equipment and control methods for safer preparations have been described [2]. Initiation of the Grignard reaction has been studied in a heat flow calorimeter [3].

Addition of part of a previous reaction mass may effect a smooth initiation [4]. An improved preparation of Grignard reagents (e.g. phenylmagnesium bromide) is described which involves the flame drying of assembled glassware in presence of iodine and magnesium to activate the latter [5]. Ether must be excluded from the vicinity during this procedure! Vent sizing calculations are given for industrial Grignard reactions [6].

Individually indexed compounds are:
∗ Bromomethane, : Metals, 0429
Butylmagnesium chloride, 1641
∗ Ethyl acetoacetate, : 2,2,2-Tris(bromomethyl)ethanol, Zinc, 2440
Ethylmagnesium bromide, 0847
Ethylmagnesium iodide, 0859
Methylmagnesium iodide, 0446
Phenylmagnesium bromide, 2225
2-Trifluoromethylphenylmagnesium bromide, 2643
3-Trifluoromethylphenylmagnesium bromide, 2643
4-Trifluoromethylphenylmagnesium bromide, 2643
See related UNIT OPERATION OR PROCESS INCIDENTS
See other HALO-ARYLMETALS

HALOACETYLENE DERIVATIVES −C≡CX

1. Whiting, M. C., *Chem. Eng. News*, 1972, **50**(23), 86
2. Brandsma, 1971, 99
3. Kloster-Jensen, E. *et al.*, *Chem. Eng. News*, 1978, **56**(19), 38
DropBooks
The tendency towards explosive decomposition noted for dihalo-2,4-hexadiyne derivatives appears to be associated more with the co-existence of halo- and acetylene functions in the same molecule, than with its being a polyacetylene. Haloacetylenes should be used with exceptional precautions [1]. Explosions may occur during distillation of bromoacetylenes when bath temperatures are too high, or if air is admitted to a hot vacuum-distillation residue [2]. Precautions necessary in isolating and handling such compounds on the small (1 g) scale are detailed [3]. Individually indexed compounds are:
Bromoacetylene, 0651
Bromochloroacetylene, 0578
1-Bromo-1,2-cyclotridecadien-4,8,10-triyne, 3599
† 3-Bromopropyne, 1090
∗ Calcium hypochlorite, : Acetylene, 3924
Chloroacetylene, 0652
4-Chloro-2-butynol, 1455
Chlorocyanoacetylene, 1036
Chloroiodoacetylene, 0598
3-Chloro-1-iodopropyne, 1073
1-Chloro-3-phenylpent-1-en-4-yn-3-ol, 4680
† 3-Chloropropyne, 1092

Copper(I) chloroacetylide, 1354
∗ 3-Cyanopropyne, 1416
Dibromoacetylene, 0582
1,4-Dibromo-1,3-butadiyne, 1351
Dichloroacetylene, 0602
1,4-Dichloro-1,3-butadiyne, 1353
1,4-Dichloro-2-butyne, 1428
1,6-Dichloro-2,4-hexadiyne, 2157
† Dicyanoacetylene, 1801
Difluoroacetylene, 0623
Diiodoacetylene, 0985
1,4-Diiodo-1,3-butadiyne, 1799
1,6-Diiodo-2,4-hexadiyne, 2173
Fluoroacetylene, 0662
Iodoacetylene, 0670
1-Iodo-1,3-butadiyne, 1381
1-Iodo-3-penten-1-yne, 1845
3-Iodo-1-phenylpropyne, 3120
3-Iodopropyne, 1105
Lithium bromoacetylide, 0580
Lithium chloroacetylide, 0599
∗ Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide, 1820
Lithium trifluoropropynide, 1046
Mercury bis(chloroacetylide), 1356
∗ Silver chloroacetylide, 0566
Silver trifluoropropynide, 1030
Sodium bromoacetylide, 0581
Sodium chloroacetylide, 0601
Tetrakis(chloroethynyl)silane, 2879
Thallium(I) iodacetylide, 0984
3,3,3-Trifluoropropyne, 1066

HALOALKANES RX

Azides

1. Suzuki, A. *et al., Bull. Chem. Soc. Jap.*, 1991, **64**(11), 3345
2. Nzeyimana, E. *et al., Progr. Aeronaut. Astronaut.* 1991, (133), 77
3. Bretherick, L., *Chem. & Ind.*, 1986, 729; *Chem. Eng. News*, 1986, **64**(51), 2

Of the lower members of this reactive group of compounds, the more lightly substituted are of high flammability like the haloalkenes. The more highly substituted find use as fire suppressants, not always with the anticipated results: Bromotrifluoromethane can promote ignition of mixtures of air and methane (but not ethane) [1]; up to 5% tetrafluoromethane accelerates detonation of hydrogen oxygen mixtures [2]. Reaction with the lighter divalent metals may give much more reactive materials analogous to Grignard reagents. Individually indexed compounds are:

Potential hazards arising from slow formation of explosive azides from prolonged contact of halogenated solvents with metallic or other azides are outlined.

See Dichloromethane: Sodium azide

∗ 1,4-Bis(1,2-dibromoethyl)benzene, 3268
∗ 1,3-Bis(trichloromethyl)benzene, 2891
∗ 1,3-Bis(trifluoromethyl)benzene, 2894
† 1-Bromobutane, 1631
† 2-Bromobutane, 1632
† Bromoethane, 0846
Bromoform, 0368
† Bromomethane, 0429
† 1-Bromo-3-methylbutane, 1984
† 1-Bromo-2-methylpropane, 1633
† 2-Bromo-2-methylpropane, 1634
† 2-Bromopentane, 1985
† 1-Bromopropane, 1241
† 2-Bromopropane, 1242
Bromotrichloromethane, 0310
3-Bromo-1,1,1-trichloropropane, 1126
Bromotrifluoromethane, 0311
∗ 2-Bromo-2,5,5-trimethylcyclopentanone, 3018
Carbon tetrabromide, 0315
Carbon tetrachloride, 0322
Carbon tetrafluoride, 0349
Carbon tetraiodide, 0525
† 1-Chlorobutane, 1637
† 2-Chlorobutane, 1638
† Chlorocyclopentane, 1923
† 1-Chloro-1,1-difluoroethane, 0731
Chlorodifluoromethane, 0369
† Chloroethane, 0848
Chloroform, 0372
† Chloromethane, 0432
† 1-Chloro-3-methylbutane, 1986
† 2-Chloro-2-methylbutane, 1987
† Chloromethyl ethyl ether, 1246
† Chloromethyl methyl ether, 0850
† 1-Chloro-2-methylpropane, 1639
† 2-Chloro-2-methylpropane, 1640
† 1-Chloropentane, 1988
† 1-Chloropropane, 1243
† 2-Chloropropane, 1244
† 1-Chloro-3,3,3-trifluoropropane, 1127
1,2-Dibromoethane, 0785
Dibromomethane, 0395

DropBooks

Dichlordifluoromethane, 0326
† *mixo*-Dichlorobutane, 1587
2,2-Dichloro-3,3-dimethylbutane, 2469
† 1,1-Dichloroethane, 0790
† 1,2-Dichloroethane, 0791
1,1-Dichloro-1-fluoroethane, 0738
† Dichloromethane, 0397
† 1,1-Dichloropropane, 1203
† 1,2-Dichloropropane, 1204
2,2-Dichloropropane, 1205
1,2-Dichlorotetrafluoroethane, 0604
† 1,1-Difluoroethane, 0801
Diiodomethane, 0400
Fluorodiiodomethane, 0373
† Fluoroethane, 0855
† Fluoromethane, 0441
Hexabromoethane, 0584
∗ 1,2,3,4,5,6-Hexachlorocyclohexane, 2306
Hexachloroethane, 0611
† 2-Iodobutane, 1647
Iodoethane, 0858
∗ 2-Iodoethanol, 0860
Iodoform, 0376
Iodomethane, 0445
† 1-Iodo-2-methylpropane, 1648
† 2-Iodo-2-methylpropane, 1649
† 2-Iodopentane, 1990
† 2-Iodopropane, 1252
Pentachloroethane, 0660
∗ Poly(carbon monofluoride), 0337
∗ Poly(chlorotrifluoroethylene), 0592
∗ Poly(tetrafluoroethylene), 0629
∗ Tetracarbon monofluoride, 1362
1,1,2,2-Tetrachloroethane, 0699
† 1,1,1-Trichloroethane, 0740
1,1,2-Trichloroethane, 0741
∗ 2,2,2-Trichloroethanol, 0744
Trichlorofluoromethane, 0330
1,1,2-Trichlorotrifluoroethane, 0606
† 1,1,1-Trifluoroethane, 0754

HALOALKENES **−C=CX**

Of the lower members of this reactive group of compounds, the more lightly substituted are of high flammability and many are classed as peroxidisable and as polymerisable compounds. Individually indexed compounds are:

† Acrylonitrile, 1107
† 1-Bromo-2-butene, 1548
† 4-Bromo-1-butene, 1549
4-Bromocyclopentene, 1884
† Bromoethylene, 0727
† 3-Bromo-1-propene, 1153
† Bromotrifluoroethylene, 0579
† 2-Chloroacrylonitrile, 1074
† 2-Chloro-1,3-butadiene, 1451
† 2-Chloro-2-butene, 1551
† 3-Chloro-1-butene, 1552
3-Chlorocyclopentene, 1885
† Chloroethylene, 0730
† 3-Chloro-2-methyl-1-propene, 1553
† 1-Chloro-1-propene, 1156
† 2-Chloropropene, 1157
† 3-Chloropropene, 1158
† Chlorotrifluoroethylene, 0591
3,5-Dibromocyclopentene, 1860
† 1,1-Dichloroethylene, 0695
† *cis*-1,2-Dichloroethylene, 0696
† *trans*-1,2-Dichloroethylene, 0697
∗ (2,2-Dichloro-1-fluorovinyl)ferrocene, 3470
† 2,3-Dichloropropene, 1132
† 1,1-Difluoroethylene, 0700
∗ 2-Ethoxy-1-iodo-3-butene, 2449
† Fluoroethylene, 0747
Hexachlorocyclopentadiene, 1808
† Hexafluoropropene, 1051
1-Iodohexa-2,4-diene, 2393
† 3-Iodopropene, 1174
∗ Methyl trifluorovinyl ether, 1101
1,2,3,-4,5-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2069
1,2,3,-5,6-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2070
Perfluorobutadiene, 1364
∗ Poly(1-pentafluorothio-1,2-butadiyne), 1379
1,1,2,3-Tetrachloro-1,3-butadiene, 1389
1,1,4,4-Tetrachlorobutatriene, 1360
Tetrachloroethylene, 0609
Tetrachloropropadiene, 1041
1,1,4,4-Tetrafluorobutatriene, 1363
† Tetrafluoroethylene, 0628
Tetraiodoethylene, 0986
† Trichloroethylene, 0656

DropBooks

† Trifluoroethylene, 0663
† 3,3,3-Trifluoropropene, 1099
See other PEROXIDISABLE COMPOUNDS

HALOANILINES **$XC_6H_4NH_2$**

Kotoyori, T., *Proc. 6th Int. Sympos. Loss Prev. Safety Prom, Proc. Ind.*, 38-1–38-16, Oslo, Norweg. Soc. Chartered Engrs., 1989

Available information on the thermal instability of halogenated anilines during vacuum distillation is presented and analysed, and the roles of dehyrohalogenation, polymerisation, salt formastion and dissociation, aerobic oxidation, corrosion and metal-catalysed decomposition are discussed. Experimental work on these topics is presented, and preventive measures proposed.

Some halo-substituted anilines are of limited thermal stability, tending to eliminate hydrogen halide which may catalyse further decomposition. To avoid decomposition during distillation, this should be conducted in the presence of solid alkali or magnesium oxide at minimum temperature (under relatively high vacuum) and/or with exclusion of air by inert gas. Individually indexed compounds are:

4-Bromoaniline, 2296
∗ 4-Bromo-1,2-diaminobenzene, 2345
2-Bromo-3,5-dimethoxyaniline, 2974
4-Bromodimethylaniline, 2973
4-Chloro-2-aminophenol, 2303
2-Chloroaniline, 2300
3-Chloroaniline, 2301
4-Chloroaniline, 2302
2-Chloro-1,4-benzenediamine, 2349
∗ 4-Chloro-1,2-benzenediamine, 2347
∗ 4-Chloro-1,3-benzenediamine, 2348
4-Chloro-2,6-diamino-*N*-methylaniline, 2822
∗ 2-Chloro-*N*-(2-hydroxyethyl)aniline, 2975
3-Chloro-4-methoxyaniline, 2795
4-Chloro-2-methylaniline, 2794
2,4-Dibromoaniline, 2226
2,4-Dichloroaniline, 2238
2,5-Dichloroaniline, 2239
3,4-Dichloroaniline, 2241
2,3,4-Trichloroaniline, 2163

HALOARENEMETAL π-COMPLEXES **$[(F_6C_6)_2M]$ etc.**

1. Klabunde, K. *et al.*, *Inorg. Chem.*, 1975, **14**, 790–791
2. Klabunde, K. *et al.*, *Angew. Chem. (Intern. Ed.)*, 1975, **14**, 288
3. Klabunde, K. *et al.*, *J. Fluorine Chem.*, 1974, **4**, 11
4. Graves, V. *et al.*, *Inorg. Chem.*, 1976, **15**, 578

The π-complexes formed between chromium(0), vanadium(0) or other transition metals, and mono- or poly-fluorobenzene show extreme sensitivity to heat and are

explosive [1,2]. Hexafluorobenzenenickel(0) exploded at 70°C [3], and presence of two or more fluorine substituents leads to unstable, very explosive chromium(0) complexes [1]. Apparently, the aryl fluorine atoms are quite labile, and on decomposition M−F bonds are formed very exothermically. Laboratory workers should be wary of such behaviour in any haloarenemetal π-complex of this type [1]. However, in later work, no indications of explosivity, or indeed of any complex formation, were seen [4]. Individually indexed compounds are:

Bis(1,n-difluorobenzene)chromium(0) isomers
Bis(fluorobenzene)chromium(0)
Bis(fluorobenzene)vanadium(0)
Bis(hexafluorobenzene)chromium(0)
Bis(hexafluorobenzene)cobalt(0)
Bis(hexafluorobenzene)iron(0)
Bis(hexafluorobenzene)nickel(0)
Bis(hexafluorobenzene)titanium(0)
Bis(hexafluorobenzene)vanadium(0)

See other HALO-ARYLMETALS

HALOARYL COMPOUNDS ArX

Though normally not very reactive, a few haloaryl compounds if sufficiently activated by other substituents or by specific reaction conditions, may undergo violent reactions. Individually indexed compounds are:

Bis(4-chlorobenzenediazo) oxide, 3456
Bis(2,4,5-trichlorobenzenediazo) oxide, 3431
∗ 1,3-Bis(trichloromethyl)benzene, 2891
∗ 1,3-Bis(trifluoromethyl)benzene, 2894
Bromobenzene, 2224
Chlorobenzene, 2228
4-Chloro-2,5-diethoxynitrobenzene, 3301
1-Chloro-2,4-dinitrobenzene, 2098
† 2-Chlorofluorobenzene, 2134
† 3-Chlorofluorobenzene, 2135
† 4-Chlorofluorobenzene, 2136
4-Chloro-2-methylphenol, 2741
2-Chloronitrobenzene, 2141
4-Chloronitrobenzene, 2142
2-Chloro-5-nitrobenzenesulfonic acid, 2144
4-Chlorotrifluoromethylbenzene, 2646
1,2-Dichlorobenzene, 2156
1,5-Dichloro-2,4-dinitrobenzene, 2077
2,4,-Dichloronitrobenzene, 2104
3,4-Dichloronitrobenzene, 2105
Dichlorophenol mixed isomers, 2161
† 1,3-Difluorobenzene, 2168
† 1,4-Difluorobenzene, 2169

DropBooks

1,5-Difluoro-2,4-dinitrobenzene, 2080
1,2-Diiodobenzene, 2172
† Fluorobenzene, 2248
∗ 1-Fluoro-2,4-dinitrobenzene, 2108
† 2-Fluorotoluene, 2747
† 3-Fluorotoluene, 2748
† 4-Fluorotoluene, 2749
Iodobenzene, 2249
2-Iodo-3,5-dinitrobiphenyl, 3450
4-Iodotoluene, 2750
1,2,4,5-Tetrachlorobenzene, 2079
† 1,2,4,5-Tetrafluorobenzene, 2081
2,4,5-Trichlorophenol, 2107
† 1,2,4-Trifluorobenzene, 2110

HALO-ARYLMETALS **ArMX, XArM**

The name adopted for this group of highly reactive (and in some circumstances intramolecularly self-reactive) compounds is intended to cover both arylmetal halides (halogen bonded to the metal) and haloaryl metals (halogen attached to the aryl nucleus). Individually indexed compounds are:

Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium, 3830
∗ Bis(cyclopentadienyl)pentafluorophenylzirconium hydroxide, 3703
Bis(pentafluorophenyl)aluminium bromide, 3418
∗ Bis(trimethylphosphine)di(3,5-dibromo-2,6-dimethoxyphenyl)nickel, 3837
3-Bromophenyllithium, 2129
4-Bromophenyllithium, 2130
3-Chlorophenyllithium, 2138
4-Chlorophenyllithium, 2139
4-Fluorophenyllithium, 2166
Pentafluorophenylaluminium dibromide, 2053
Pentafluorophenyllithium, 2059
Tetrakis(pentafluorophenyl)titanium, 3842
2-Trifluoromethylphenyllithium, 2655
3-Trifluoromethylphenyllithium, 2656
4-Trifluoromethylphenyllithium, 2657
2-Trifluoromethylphenylmagnesium bromide
3-Trifluoromethylphenylmagnesium bromide
4-Trifluoromethylphenylmagnesium bromide

See GRIGNARD REAGENTS
HALOARENEMETAL π-COMPLEXES
ORGANOLITHIUM REAGENTS

HALOBORANES **−BHX, $-BX_2$**

The degree of reactivity to air or to water depends on the degree of substitution of hydrogen by halogen. This highly reactive group includes the individually indexed compounds:

Bromodiborane, 0159
1-Bromopentaborane(9), 0186
Chlorodiborane, 0160
∗ *B*-Chlorodimethylaminodiborane, 0962
Diboron tetrachloride, 0161
Diboron tetrafluoride, 0162
1,2-Dibromopentaborane(9), 0187
Iododiborane, 0165
Tetraboron tetrachloride, 0179

See related NON-METAL HALIDES, NON-METAL HYDRIDES

HALOCARBONS **RX, ArX**

This generic name often to be found in the text is used in the sense of halogen-substituted hydrocarbons which may also contain hydrogen, i.e. substitution may not necessarily be complete. It represents a range of halogenated aliphatic or aromatic compounds widely used in research and industry, often as solvents or diluents. None are completely inert chemically, but in general, reactivity decreases with increasing substitution of hydrogen by halogen (particularly with fluorine), in both saturated and unsaturated hydrocarbons.

Several lower partially halogenated hydrocarbons (dichloromethane, bromomethane, trichloroethylene, 1,1,1-trichloroethane) have no measurable flash point, but are nonetheless capable of forming flammable and explosive mixtures with air, and several such accidents are recorded.

DropBooks

See entry FLASH POINTS (reference 19)
CHLOROFLUOROCARBONS
FLUOROCARBONS
HALOALKANES
HALOALKENES
HALOARYL COMPOUNDS

See METAL–HALOCARBON INCIDENTS
Pentaborane(9), : Reactive solvents, 0188
Calcium disilicide, : Carbon tetrachloride, 3944
Fluorine, : Halocarbons, 4310
Disilane, : Non-metal halides, 4569
Dinitrogen tetraoxide, : Halocarbons, 4747
Oxygen (Liquid), : Halocarbons, 4832

HALOGENATION INCIDENTS

Examples of incidents involving halogenation reactions are:
Bromine, : Alcohols, 0261
Bromine, : Aluminium, Dichloromethane, 0261

Bromine, : Isobutyrophenone, 0261
N-Bromosuccinimide, : Dibenzoyl peroxide, 4-Toluic acid, 1425
Chlorine, 4047
Chlorine, : Antimony trichloride, Tetramethylsilane, 4047
Chlorine, : 2-Chloroalkyl aryl sulfides, Lithium perchlorate, 4047
Sulfur tetrafluoride, : 2-(Hydroxymethyl)furan, Triethylamine, 4350
Titanium, : Halogens, 4919
Trifluoromethanesulfenyl chloride, : Chlorine fluorides, 0322
ALKYLALUMINIUM DERIVATIVES: Halocarbons
BORANES: Carbon tetrachloride
N-HALOIMIDES: Xylene
SILANES: Chloroform
See other UNIT PROCESS INCIDENTS

HALOGEN AZIDES XN_3

Metals, or Phosphorus
Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1967, **6**, 240
A comprehensive review covers stability relationships and reactions of these explosive compounds and their derivatives. Bromine, chlorine and iodine azides all explode violently in contact with magnesium, zinc or white phosphorus.

Individually indexed compounds are:
Bromine azide, 0256
Chlorine azide, 4030
∗ Cyanogen azide, 0544
Fluorine azide, 4307
Iodine azide, 4621
See METAL PNICTIDES
See other *N*-HALOGEN COMPOUNDS, NON-METAL AZIDES

N -HALOGEN COMPOUNDS −NX

1. Kovacic, P. *et al., Chem. Rev.*, 1970, **70**, 640
2. Petry, R. C. *et al., J. Org. Chem.*, 1967, **32**, 4034
3. Freeman, J. P. *et al., J. Amer. Chem. Soc.*, 1969, **91**, 4778
4. Guillamin, J. C. *et al., Synthesis*, 1985, (12), 1131–1133
5. Guillamin, J. C. *et al.,Tetrahedron*, 1988, **44**, 4431–4446; 4447–4455
6. Kirk-Othmer, 1993, (4th Edn) Vol IV, 917, 921

Many compounds containing one or more N−X bonds show unstable or explosive properties (and are also oxidants), and this topic has been reviewed [1]. Difluoroamino compounds, ranging from difluoramine and tetrafluorohydrazine to polydifluoroamino compounds, are notably explosive and suitable precautions have been detailed [2,3]. Preparative scale *N*-chlorination of 1y and 2y amines by passing them over *N*-chlorosuccinimide is described. In presence of alumina, 1y amines give the *N,N* -dichloro derivatives. The products must be handled with

great caution, and collection and storage at −30°C is recommended, as some of the products exploded at ambient temperature [4]. The range of compounds so prepared has been further extended [5]. *N*-Halosulfinylamines (O=S=NHal) are stable at room temperature but react explosively with water. Dialkyldichlorosulfurdiimides [$R2S(=NCl)_2$] explode violently when heated [6].

Within this class fall the separate groups:

N-CHLORONITROAMINES
DIFLUOROAMINO COMPOUNDS
HALOGEN AZIDES
N-HALOIMIDES
N,N,N′-TRIFLUOROALKYLAMIDINES

Individually indexed compounds are:

Azidoiodoiodonium hexafluoroantimonate, 4361
Azo-*N*-chloroformamidine, 0792
Benzoquinone 1,4-bis(chloroimine), 2159
1,4-Benzoquinone-4-chloroimine, 2140
4,4-Bis(difluoroamino)-3-fluoroimino-1-pentene, 1867
Bromamine, 0249
N-Bromoacetamide, 0784
1-Bromoaziridine, 0783
3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2645
N-Bromo-3-nitrophthalimide, 2884
N-Bromosuccinimide, 1425
N-Bromotetramethylguanidine, 2002
N-Bromotrimethylammonium bromide(?), 1300
Chloramine, 4000
∗ Chloriminovanadium trichloride, 4165
N-Chloroacetamide, 0789
N-Chloroallylamine, 1202
N-Chloro-3-aminopropyne, 1129
N-Chloro-3-aminopropyne, 1129
1-Chloroaziridine, 0786
1-Chlorobenzotriazole, 2150
N-Chloro-bis(2-chloroethyl)amine, 1590
N-Chlorobis(trifluoromethanesulfonyl)imide, 0596
N-Chlorocinnamaldimine, 3126
N-Chlorodimethylamine, 0895
N-Chloro-4,5-dimethyltriazole, 1490
N-Chloro-4-methyl-2-imidazolinone, 1554
N-Chloro-5-methyl-2-oxazolidinone, 1488
N-Chloro-3-morpholinone, 1489
N-Chloro-4-nitroaniline, 2231
N-Chloro-5-phenyltetrazole, 2674
N-Chloropiperidine, 1948
N-Chloropyrrolidine, 1584

DropBooks

N-Chlorosuccinimide, 1427
N-Chlorotetramethylguanidine, 2004
Diamminedichloroamidotrichloroplatinum(IV), 4179
2,6-Dibromobenzoquinone-4-chloroimide, 2076
Dichloramine, 4063
N,*N*-Dichloro-β-alanine, 1168
1-Dichloroaminotetrazole, 0371
N,*N*-Dichloroaniline, 2242
2,6-Dichlorobenzoquinone-4-chloroimide, 2078
N,*N*′-dichlorobis(2,4,6-trichlorophenyl)urea, 3596
Dichlorofluoramine, 4059
N,*N*-Dichloroglycine, 0739
N,*N*-Dichloromethylamine, 0437
N,*N*-Dichloropentafluorosulfanylamine, 4060
Difluoramine, 4311
3-Difluoroamino-1,2,3-trifluorodiaziridine, 0358
∗ Difluoroammonium hexafluoroantimonate, 4380
Difluoroammonium hexafluoroarsenate, 0098
Difluorodiazene, 4314
Difluoro-*N*-fluoromethanimine, 0344
Diiodamine, 4426
Dimethyl *N*,*N*-dichlorophosphoramidate, 0901
1,1-Dimethylethyldibromamine, 1636
Ethyl *N*-chloro-*N*-sodiocarbamate, 1159
Fluoramine, 4296
1-Fluoroiminohexafluoropropane, 1058
2-Fluoroiminohexafluoropropane, 1059
N-Fluoroiminosulfur tetrafluoride, 4357
N-Fluoro-*N*-nitrobutylamine, 1645
3-Fluoro-3-(trifluoromethyl)-3*H*-diazirine, 0631
∗ Iodine isocyanate, 0524
Nitrogen chloride difluoride, 3978
Nitrogen tribromide hexaammoniate, 0290
Nitrogen trichloride, 4724
Nitrogen trifluoride, 4336
Nitrogen triodide, 4633
Nitrogen triiodide–silver amide, 4634
Nitrogen triiodide–ammonia, 4635
Nitrosyl chloride, 4023
Nitrosyl fluoride, 4302
Nitryl chloride, 4025
Nitryl fluoride, 4303
∗ Pentafluoroguanidine, 0359
Sodium *N*-chlorobenzenesulfonamide, 2229
Sodium *N*-chloro-4-toluenesulfonamide, 2739
N,*N*,*N*″,*N*″-Tetrachloroadipamide, 2370

Tetrafluoroammonium hexafluoromanganate, 4384
Tetrafluoroammonium hexafluoronickelate, 4385
Tetrafluoroammonium octafluoroxenate, 4386
Tetrafluoroammonium perbromate, 0242
Tetrafluoroammonium perchlorate, 3986
Tetrafluoroammonium tetrafluoroborate, 0133
Tetrafluorodiaziridine, 0351
† Tetrafluorohydrazine, 4345
Tetrakis(*N,N* -dichloroaminomethyl)methane, 1900
Tribromamine oxide, 0291
1,3,5-Trichloro-2,4,6-trifluoroborazine, 0173
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazine, 4145
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazinemolybdenum, 4142
Trifluoroacetyliminoiodobenzene, 2903
2,4,6-Tris(bromoamino)-1,3,5-triazine, 1091
2,4,6-Tris(dichloroamino)-1,3,5-triazine, 1043

HALOGEN OXIDES XO_n

Of the various compounds arising from union of oxygen with one or more halogens, many are endothermic and all are generally unstable but powerful oxidants.

Individually indexed compounds are:
Bromine bromate, 0276
Bromine dioxide, 0258
Bromine perchlorate, 0235
Bromine trioxide, 0259
Bromyl fluoride, 0239
Chlorine dioxide, 4042
Chlorine perchlorate, 4101
Chlorine trifluoride oxide, 3982
Chlorine trioxide, 4044
Chloryl hypofluorite, 3973
Chloryl perchlorate, 4104
Dichlorine oxide, 4095
Dichlorine trioxide, 4100
∗ Dicyanogen *N,N′*-dioxide, 0998
Dioxygen difluoride, 4320
Fluorine perchlorate, 3976
Hexaoxygen difluoride, 4327
Iodine dioxide trifluoride, 4334
Iodine(V) oxide, 4627
Iodine(VII) oxide, 4628
Oxygen difluoride, 4317
Perbromyl fluoride, 0240
Perchloryl fluoride, 3974

DropBooks

Perchloryl perchlorate, 4107
Tetrafluoroiodosyl hypofluorite, 4356
'Trioxygen difluoride', 4323

HALOGENS X_2

The reactivity hazards of this well defined group of oxidants towards other materials decrease progressively from fluorine, which reacts violently with most materials (except for those metals on which resistant fluoride films form), through chlorine and bromine to iodine. Astatine may be expected to continue this trend. The individual entries are:
Bromine, 0261
Chlorine, 4047
Fluorine, 4310
Iodine, 4625

***N*-HALOIMIDES** **−CO.N(X)CO.−**

Alcohols, or Amines, or Diallyl sulfide, or Hydrazine, or Xylene
Martin, R. H., *Nature*, 1951, **168**, 32
Many of the reactions of *N*-chloro- and *N*-bromo-imides are extremely violent or explosive. Those observed include *N*-chlorosuccinimide with aliphatic alcohols or benzylamine or hydrazine hydrate; *N*-bromosuccinimide with aniline, diallyl sulfide, or hydrazine hydrate; or 3-nitro-*N*-bromophthalimide with tetrahydrofurfuryl alcohol; 1,3-dichloro-5,5-dimethyl-2,4-imidazolidindione with xylene (violent explosion). Individually indexed compounds are:
N-Bromosuccinimide, 1425
Chloriminovanadium trichloride, 4165
N-Chlorosuccinimide, 1427
1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione, 1865
Potassium 1,3-dibromo-1,3,5-triazine-2,4-dione-6-oxide, 0132
Sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide, 1037
1,3,5-Trichloro-1,3,5-triazinetrione, 1039
See other *N*-HALOGEN COMPOUNDS

2-HALOMETHYL-FURANS OR -THIOPHENES

Heterocyclic Compounds, Vol. 1, 207, Elderfield, R. C. (Ed.), New York, Wiley, 1950
The great instability of 2-bromomethyl- and 2-chloromethyl-furans, often manifest as violent or explosive decomposition on attempted distillation, is reviewed. The furan nucleus is sensitive to traces of halogen acids, and decomposition becomes autocatalytic. Individually indexed compounds are:
2,5-Bis(chloromethyl)thiophene, 2305
2-Bromomethylfuran, 1840
2-Bromomethyl-5-methylfuran, 2346

2-Chloro-5-chloromethylthiophene, 1830
2-Chloromethylfuran, 1841
2-Chloromethyl-5-methylfuran, 2352
2-Chloromethylthiophene, 1842
See also BENZYL COMPOUNDS

HALOPHOSPHINES **$-PHX$, $-PX_2$**

The degree of reactivity towards air or to water depends upon the degree of substitution of hydrogen by halogen. Individually indexed compound are:

∗ Phosphorus azide difluoride, 4315
Phosphorus trifluoride, 4339
Phosphorus triiodide, 4636
Tetrachlorodiphosphane, 4171
Tetraiododiphosphane, 4637

See related NON-METAL HALIDES, NON-METAL HYDRIDES

HALOSILANES **Si_mX_n**

1. Schumb, W. C. *et al., Inorg. Synth.*, 1939, **1**, 46
2. Halvorsen, F. *et al., Proc. 29th Annu. Loss Prev. Symp.*, 1995, paper 6B (Amer. Inst. Chem. Engineers)

When heated, the vapours of the higher chlorosilanes (hexachlorodisilane to dodecachloropentasilane) ignite in air. Other halo- and haloalkyl-silanes ignite without heating or have low flash points: some react violently with water [1]. An account has been given of cleaning and dismantling a plant contaminated with shock sensitive and polymeric 'oil silanes' arising as byproducts from trichlorosilane handling [2]. Individually indexed compounds are:

DropBooks

† Bromosilane, 0250
Decachlorotetrasilane, 4197
† Dichlorosilane, 4066
Dodecachloropentasilane, 4198
Fluorosilane, 4298
Hexachlorodisilane, 4191
Iododisilane, 4543
Octachlorotrisilane, 4194
∗ Poly(difluorosilylene), 4330
Tetrachlorosilane, 4173
† Tribromosilane, 0287
† Trichlorosilane, 4136
† Trifluorosilane, 4333

See related NON-METAL HALIDES, NON-METAL HYDRIDES

HAZARDOUS MATERIALS

1. Cloyd, D. R. *et al., Handling Hazardous Materials*, NASA Tech. Survey SP-5032, Washington, NASA, 1965

2. *Fire Protection Guide on Hazardous Materials*, SPP-1C, Boston (Ma.), NFPA, 6th edn., 1975

The survey of hazards and safety procedures involved in handling rocket fuels and oxidisers includes liquid hydrogen, pentaborane, fluorine, chlorine trifluoride, ozone, dinitrogen tetraoxide, hydrazine, methyl hydrazine and 1,1-dimethyl hydrazine [1]. The later volume [2] is a bargain compendium of five NFPA publications:

325A, *Flashpoint Index of Tradename Liquids* (8800 items), 1972

325M, *Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids* (1300 items), 1969

49, *Hazardous Chemicals Data* (416 items), 1975

491M, *Manual of Hazardous Chemical Reactions* (3550 items), 1975

704M, *Recommended System for Identification of Fire Hazards of Materials*, 1975

HAZARDS FROM PRESSURE

Hazards from Pressure: Exothermic Reactions, Unstable Substances, Pressure Relief and Accidental Discharge, Gibson, N. (ed.), IChE Symp. Ser. No. 102, Oxford, Pergamon, 1987

The 1986 UK Symposium covered hazards from pressure effects originating in various ways from exothermic runaway reactions and unstable substances, and the measures necessary to mitigate these effects. Some of the reactive hazards involved may be found under the entries:

Copper(II) acetylide(reference 2), 0615

2-Hydroxyethylamine: Carbon dioxide, etc., 0943

Sodium dithionite (reference 2), 4807

BLOWING AGENTS (reference 2)

HEAT FLOW CALORIMETRY (reference 5)

See PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

HEAT FLOW CALORIMETRY

1. Hub, L., *Proc. 6th Symp. Chem. Proc. Hazards*, Symp. Ser. No. 49, 39–46, Rugby, IChE, 1977
2. Brogli, F. *et al., Runaway Reactions*, Paper 3/M, 1–10
3. Fierz, H. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Process Ind.*, Vol. 3, A12–A21, Rugby, IChE, 1983
4. Stockton, G. W. *et al.*, Euro-pat. Appl. EP 170713, 1986
5. Wright, T. K. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 85–96, Oxford, Pergamon, 1987
6. Burke, P. E. *Spec. Publ. -R. Soc. Chem., 195(Pilot Plants and Scale-up of Chemical Processes)*, 1997, 52
7. Cardillo, P. *et al., Afinidad*, 1998, **55**(474), 115

As an alternative and complementary technique to the study of chemical materials by DTA, DSC, or ARC, the study of chemical processes in miniature reactors has been developed. Equipment which is sufficiently instrumented to permit full

analysis of processing heat flows arising from reaction exotherms or process deviations is available, in two variants. Both have accurately controlled heating and cooling systems which are used separately or simultaneously to maintain the stirred reactor temperature at the desired level as reaction proceeds, and to indicate the heat flows from the liquid phase to the jacket and from the vapour phase to the reflux condenser etc. The first variant uses a glass flask reactor of 2 l capacity fitted with stirrer, doser and reflux condenser and can operate between -30° to $+200^{\circ}$C under vacuum or at atmospheric pressure. Further details of the reaction safety calorimeter (RSC) and of its application to various processing problems are published [1]. The second variant has interchangeable glass vessels of 0.5 to 2.5 l operable between -20 to $+200^{\circ}$C at up to 3 bar internal pressure, and operation and application of the bench scale calorimeter (BSC) to several different processing problems and investigations has been discussed [2,3]. Improved design features claimed include use of a zirconium reaction vessel rather than glass (10^3 increase in thermal conductivity), thermostatted feed streams and adiabatic shield [4]. The design and use of an isothermal heat flow calorimeter to assess cooling and other processing reqirements for safe operation of (semi-)batch processes are discussed. Use of this simpler type of calorimeter is complementary to that of the more expensive variable heat flow calorimeters [5].

In the 1990s, reaction calorimetry has found extensive use in industrial scale-up operations. The editor's limited exposure to it suggests that the commercially available equipment has indifferent agitation and may in consequence handle multiphase reactions poorly: anathema though they be to academic kineticists, industry finds slurries attractive. However it is a simple technique by which to acquire data on the kinetics of heat production. Publications have become very numerous, mostly publicity from testing houses offering the service. Some very recent work is found in [6], [7].

See CALORIMETRY

DropBooks

HEAT TRANSFER

1. Bourne, J. R. *et al., Chem. Eng. Sci.*, 1987, **42**, 2183–2192
2. Bourne, J. R. *et al., Chem. Eng. Sci.*, 1987, **42**, 2193–2196

The factors which affect heat transfer from an exothermic fluid reaction system are important in determining whether a runaway reaction (thermal explosion) will ensue. Agitation reduces local heat acumulation and applied cooling affects overall heat retention and temperature of the reactor contents. Studies in unstirred vertical cylinder reactors showed the effects of convection in modifying the temperature- and flow-fields existing in a conduction-only system. An analogy between the temperature profiles in active (exothermally reacting) systems and passive (cooling without reaction) systems at equal heat-removal rates was established, offering the possibility of simpler and safer experimental assessments [1]. Correlations in a freely conducting active system show that the maximum temperature occurs just below the liquid surface, and to avoid thermal runaway, the temperature must not exceed a critical value, which depends on the heat generation rate, the liquid physical properties and the vessel size [2].

See 1,2,4,5-Tetrachlorobenzene: Sodium hydroxide, etc. (references 10, 11)

HEAVY METAL DERIVATIVES

This class of compounds showing explosive instability deals with heavy metals bonded to elements other than nitrogen and contains the separately treated groups:

GOLD COMPOUNDS
LEAD SALTS OF NITRO COMPOUNDS
LITHIUM PERALKYLURANATES
MERCURY COMPOUNDS
METAL ACETYLIDES
METAL FULMINATES
METAL OXALATES
PLATINUM COMPOUNDS
PRECIOUS METAL DERIVATIVES
SILVER COMPOUNDS

as well as the individually indexed compounds:

Barium acetate, 1486
Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-N3,N5]-(T-4) cobalt, 3868
Cadmium propionate, 2418
∗ Cobalt(II) picramate, 3460
Copper(I) chloroacetylide, 1354
Diacetatotetraaquocobalt, 1780
Dicopper(I) ketenide, 0621
∗ Diethyllead dinitrate, 1692
Dimethylmethyleneoxosulfanenickel(0) diethylene complex, 2856
Dinitrosylnickel, 4741
∗ Hydroxycopper(II) glyoximate, 0799
Iron(II) maleate, 1393
Iron(III) maleate, 3447
Lanthanum 2-nitrobenzoate, 3815
Lead 2-amino-4,6-dinitrophenoxide, 3469
Lead bromate, 0278
Lead hyponitrite, 4745
Lead(II) nitrate phosphinate, 4468
Lead oleate, 3895
Lead(II) phosphinate, 4531
Lead(II) phosphite, 4535
Lead(II) picrate, 3436
∗ Lead(II) thiocyanate, 1000
Lead 2,4,6-trinitroresorcinoxide, 2071
Lead(II) trinitrosobenzene-1,3,5-trioxide, 3594
Manganese(II) phosphinate, 4519
Manganese picrate hydroxide, 3742
Nickel 2,4-dinitrophenoxide hydroxide, 3745
Nickel 2-nitrophenoxide, 3464
Nickel picrate, 3435

∗ 5-Nitrosalicylhydrazide, 2778
Scandium 3-nitrobenzoate, 3816
Silver osmate, 0034
Thallium bromate, 0260
Thallium(I) methanediazoate, 0458
Thallium(I) 2- or 4-nitrophenoxide, 2187
Thallium *aci*-phenylnitromethanide, 2723

See also METAL AZIDES, METAL CYANIDES (AND CYANO COMPLEXES), *N*-METAL DERIVATIVES

HETEROCYCLIC *N*-SULFINYLAMINES **Het-N=S=O**

Butler, R. N. *et al.*, *Chem. & Ind.*, 1986, 750; J. Chem. Soc., Perk. Trans. 2, 1989, 1855

A range of the title compounds were prepared by treating the amines with sulfinyl chloride in benzene. Purification by vacuum distillation led to violent explosions of some of those with 5 membered rings containing two or more heteroatoms on a number of occasions. It is essential to keep the distillation temperature below 60°C.

See other N–S COMPOUNDS

HEXAFLUOROCHLORONIUM SALTS **$[ClF_6]^+$ Z^-**

1. Christe, K. O., *Inorg. Chem.*, 1973, **12**, 1582
2. Roberts, F. Q., *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 737

These are very powerful oxidants and react explosively with organic materials or water [1]. They are not in themselves explosive, contrary to an earlier report [2].

See other OXIDANTS

DropBooks

HEXAMETHYLNITRATODIALUMINATE SALTS **M^+ $[Al_2(Me)_6NO_3]^-$**

Atwood, J. L. *et al.*, *J. Organomet. Chem.*, 1978, **155**, 2

In the series of air-sensitive title salts, the potassium, rubidium or caesium salts ignite on exposure to air, and the tetramethyl- or tetraethyl-ammonium salts ignite with violence.

See other PYROPHORIC MATERIALS

HIGH-NITROGEN COMPOUNDS

Benson, F. R., *The High-Nitrogen Compounds*, New York, Wiley-Interscience, 1984

The major portion of the book (Ch. 2, pp 2–262) deals with the thermal stability of groups of these compounds in a series of tables.

This class heading is intended to include not only those compounds containing a high total proportion of nitrogen (up to ~90%) but also those containing high local concentrations in substituent groups (notably azide, diazo and diazonium) within the molecule. Many organic molecular structures containing several chain-linked

atoms of nitrogen are unstable or explosive and the tendency is exaggerated by attachment of azide or diazonium groups, or a high-nitrogen heterocyclic nucleus. Closely related but separately treated classes and groups include:

AZIDES (in several groups)
DIAZOAZOLES
DIAZO COMPOUNDS
DIAZONIUM SALTS (in several groups)
HYDRAZINIUM SALTS
N-NITRO COMPOUNDS
TETRAZOLES
TETRAZENES
TRIAZENES
TRIAZOLES

Individually indexed compounds are:

1-Acetyl-4-(4′-sulfophenyl)-3-tetrazene, 2982
Aluminium azide, 0082
Aluminium tetraazidoborate, 0059
Aminoguanidine, 0507
1-Amino-3-nitroguanidine, 0495
5-Aminotetrazole, 0461
5-Amino-1,2,3,4-thiatriazole, 0413
4-Amino-4*H*-1,2,4-triazole, 0812
Ammonium azide, 4526
Azidoacetonitrile, 0714
Azido-2-butyne, 1473
2,2′-Azobis(2-amidiniopropane) peroxodisulfate
3,3′-Azo-(1-nitro-1,2,4-triazole), 1401
Benzotriazole, 2269
1,3-Bis(5-amino-1,3,4-triazol-2-yl)triazene, 1576
Bis(1-benzo[*d*]triazolyl) carbonate, 3598
Bis(1-benzo[*d*]triazolyl) oxalate, 3629
Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-N3,N5]-(T-4) cobalt, 3868
1,6-Bis(5-tetrazolyl)hexaaza-1,5-diene, 0827
3,4-Bis(1,2,3,4-thiatriazol-5-ylthio)maleimide, 2073
5-*tert*-Butyl-3-diazo-3*H*-pyrazole, 2831
Carbonic dihydrazide, 0508
Cyanodiazoacetyl azide, 1346
Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1429
5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1345
Cyanoguanidine, 0813
Cyanohydrazonoacetyl azide, 1083
2,3-Diazido-1,3-butadiene, 1437
1,2-Diazidocarbonylhydrazine, 0720
Diazidomethyleneazine, 1021

Diazidomethylenecyanamide, 1017
2,3-Diazidopropiononitrile, 1121
2,6-Diazidopyrazine, 1400
2-Diazo-2H-imidazole, 1082
2-Diazonio-4,5-dicyanoimidazolide, 2050
3-Diazoniopyrazolide-4-carboxamide, 1399
3-Diazo-5-phenyl-3*H*-pyrazole, 3118
4-Diazo-5-phenyl-1,2,3-triazole, 2910
3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2909
4-Diazo-1,2,3-triazole, 0678
3-Diazo-3*H*-1,2,4-triazole, 0677
1,5-Diphenylpentaazadiene, 3507
5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3677
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1853
1-Ethyl-1,1,3,3-tetramethyltetrazenium tetrafluoroborate, 2586
Formylhydrazine, 0473
1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1.3.5-triphosphorine, 4795
Hydrazinium azide, 4550
Hydrazinium chloride, 4007
5-Hydrazino-1,2,3,4-thiatriazole, 0462
5,5′-Hydrazotetrazole, 0826
1-Hydroxybenzotriazole, 2272
1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0817
∗ Lithium hexaazidocuprate(4−), 4278
∗ Lithium tetraazidoaluminate, 0081
∗ Lithium tetraazidoborate, 0151
Methyl 3,3-diazido-2-cyanoacrylate, 1824
Methylenebis(3-nitramino-4-methylfurazan), 2805
1-Methyl-1,2,3-triazole, 1189
Nitrosyl azide, 4766
3-Nitro-1,2,4-triazolone, 0716
Pentazole, 4443
3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2804
N-Phenyl-1,2,3,4-thiatriazolamine, 2729
Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide
Sodium 5-azidotetrazolide, 0551
∗ Sodium hexaazidophosphate, 4794
Tetraallyl-2-tetrazene, 3545
∗ *trans*-Tetraamminediazidocobalt(III) *trans*-diamminetetraazido-cobaltate(1−)
Tetraazido-1,4-benzoquinone, 2633
Tetraimide, 4527
1,3,4,6-Tetrakis(2-methyltetrazol-5-yl)-hexaaza-1,5-diene, 3013
Tetramethyl-2-tetrazene, 1759
1,3,6,8-Tetraphenyloctaazatriene, 3849
1,2,4,5-Tetrazine, 0715

DropBooks

2,4,6-Triazido-1,3,5-triazine, 1348
1,2,4-Triazole-3-diazonium nitrate, 0680
1,3,5-Triphenyl-1,4-pentaazadiene, 3754

HIGH PRESSURE REACTION TECHNIQUES

1. Rooymans, C. J. M. in *Preparative Methods in Solid State Chemistry*, Hagenmuller, P. (Ed.), New York, Academic Press, 1972
2. *High Pressure Safety Code*, London, High Pressure Association, 1975
3. Paauwe, J., *High Press. Technol.*, 1977, **1**, 13–28
4. Jercinovic, L. M., *Plant/Oper. Progr.*, 1984, **3**, 34–37
5. Mehne, P. H., *Plant/Oper. Progr.*, 1984, **3**, 37–39
6. Franko-Filipasic, B. R. *et al., Chem. Eng. Progr.*, 1984, **8** 0(3), 65–69
7. Livingston, E. H., *Chem. Eng. Progr.*, 1984, **80**(3), 70–75
8. Sherman, W. F., *Experimental Techniques in High-pressure Research*, New York, Wiley, 1987

The chapter which reviews high-pressure (HP) techniques in liquid and gas systems for preparative purposes also includes safety considerations [1]. The Code deals mainly with mechanical hazards, but attention is drawn to the fact that application of HP to chemical systems may influence stability adversely [2]. The forces and energy involved in HP systems, and the causes and elimination of accidents in HP operations are reviewed [3]. Design procedures and checklists [4] and training methods [5] relevant to safety in HP operations are discussed. The design features of two HP resesarch laboratories are detailed, including use of remote manipulation for hazardous reaction studies [6]. Operational factors to minimise hazards in HP facilities, including operator training, equipment inspection and maintenance, are presented [7]. A new handbook deals with the design, construction and safe operation of equipment for research at high pressures [8].

HIGH RATE DECOMPOSITION

Gibson, N. *et al., Runaway Reactions*, 1981, Paper 3/R, 1–14

Some compounds not classified as deflagrating or detonating explosives can decompose violently (deflagrate), and account of this must be taken in designing powder handling plant, which is now usually totally confined. Compounds of this type, often with an oxygen balance around −200, usually decompose when heated with a high rate of decomposition. Those compounds below were examined for ease of initiation when exposed to friction or localised heating, in both open or closed systems. Individually indexed compounds are:

2-Acetylamino-3,5-dinitrothiophene, 2280
2-Amino-3,5-dinitrothiophene, 1421
1,5-(or 1,8-)Bis(dinitrophenoxy)-4,8-(or 4,5-)dinitroanthraquinone, 3860
2-Bromo-4,6-dinitroaniline, 2132
4-Bromo-2,6-dinitroaniline, 2133
2-Chloro-4,6-dinitroaniline, 2153
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1954

2-Formylamino-3,5-dinitrothiophene, 1823
2-Hydroxy-6-nitro-1-naphthalenediazonium-4-sulfonate, 3240
2-Methoxyanilinium nitrate, 2829
See entries CRITICAL IGNITION TEMPERATURE, DEFLAGRATION INCIDENTS

HIGH SURFACE-AREA SOLIDS

Smith, E. A., *Processing*, 1977, (11), 35–37
The reactivity of solids may change dramatically as they are ground to sub-micron sizes. Graphite becomes pyrophoric at 400 m^3/g, and if ground under nitrogen to 600 m^3/g, cyanogen is produced by direct combination of the elements. Sulfur becomes highly reactive at lower micron sizes, and iron becomes liable to explosive oxidation when ground to below 1 μ. Theoretical aspects of the great increase in surface energy are discussed.

HIGH VALENCY METAL FLUORIDES

Dukat, W. W., *et al., J. Chem. Soc., Chem. Comm.*, 1993, (18), 1429
High valency transition metal fluorides may react violently with organic materials, not only by fluorinating, C-H bonds but also by exchange reactions with organochlorine compounds. Thus osmium and iridium hexafluorides reacted explosively with a fewfold excess of dichloromethane, unless judiciously cooled with liquid nitrogen, even at sub-gram scale. Such compounds usually also react vigorously with water and other nucleophiles (Editor's comment).

DropBooks

HOPCALITE

Kirk-Othmer, 1996, Vol. 17, 216
An oxidation catalyst containing cobalt, copper, manganese and silver species. It adsorbs nitroalkanes strongly, which may then ignite. Respirator cartridges containing it should not be used in high concentrations of nitroalkanes.
See NITROALKANES

HYDRAZINE METAL MALONATES AND SUCCINATES

1. Sivasankar, B. N. *et al., Synth. React. Inorg. Met.-Org. Chem.*, 1994, **24**(9), 1573
2. Sivasankar, B. N. *et al., Mater. Res. Bull.*, 1996, **31**(1), 47

Several octahedral dihydrazine metal (II) salts of this class were prepared and thermally decomposed. The succinates and malonates of nickel and cadmium decomposed explosively [1]. A later paper on mixed metal bis-hydrazine malonates of cobalt with magnesium, manganese, nickel, zinc or cadmium recommends that decomposition, in a pre-heated crucible at 500°C, be of small quantities only. The same workers have reported exothermic decomposition of similar hydrazine complexed salts of other small organic acids.

Individual Compounds are:
Dihydrazinecadmium(II) malonate, 1324
Dihydrazinecadmium(II) succinate, 1741
Dihydrazinenickel(II) malonate, 1328
Dihydrazinenickel(II) succinate, 1760
See also AMMINEMETAL OXOSALTS

HYDRAZINEMETAL NITRATES $[(H_4N_2)_mM][NO_3]_n$

1. Médard, L. *et al.*, *Mém. Poudres*, 1952, **34**, 159–166
2. Patel, K. C. *et al*, *Synth. React. Inorg. Met.-Org. Chem.*, 1982, **12**(4), 383
Hydrazine complexes of cadmium, cobalt, manganese, nickel and zinc nitrates were prepared as possible initiator materials. Dihydrazinemanganese(II) nitrate ignites at 150°C but is not shock-sensitive, while trihydrazinecobalt(II) nitrate, which decomposes violently at 206–211°C or in contact with conc. acids, and trihydrazinenickel(II) nitrate (deflagrates at 212–215°C) are fairly shock-sensitive. Trihydrazinecadmium nitrate (defl. 212–245°C) and trihydrazinezinc nitrate are of moderate and low sensitivity, respectively [1]. A later study covers the same ground, adding trihydrazineiron(II) nitrate and dihydrazinecadmium(II) nitrates to the list of potential primary explosives, but reporting the dihydrazinemagnesium salt as not shock-sensitive. This work also covered some dihydrazinemetal azides and perchlorates, those of Mg were not shock sensitive but the azides of Co, Ni, and Zn were [2]. The combination of an endothermic fuel, an oxidant and catalytic metals–mostly having 1 electron transitions capable of initiating radical reactions–might be predicted to be sensitive.
See Trihydrazinenickel(II) nitrate
See other AMMINEMETAL OXOSALTS

HYDRAZINIUM SALTS $H_2NN^+H_3Z^-$

1. Mellor, 1940, Vol. 8, Suppl. 2.2, 84–86
2. Salvadori, R., *Gazz. Chim. Ital. [2]*, 1907, **37**, 32
3. Levi, G. R., *Gazz. Chim. Ital. [2]*, 1923, **53**, 105
Several salts are explosively unstable, including hydrazinium azide (explodes on rapid heating or on initiation by a detonator, even when damp), chlorate (explodes at m.p., 80°C), chlorite (also highly flammable when dry), hydrogen selenate, hydrogen sulfate (explodes when melted), nitrate, nitrite, and the highly explosive perchlorate and diperchlorate used as propellants [1,2,3].

Some examples are:
1,1-Diphenylhydrazinium chloride, 3519
Hydrazinium azide, 4550
Hydrazinium chlorate, 4010
Hydrazinium chloride, 4007
Hydrazinium chlorite, 4008
Hydrazinium dinitrate, 4561
Hydrazinium diperchlorate, 4068

Hydrazinium hydrogen selenate, 4558
Hydrazinium nitrate, 4549
Hydrazinium nitrite, 4548
Hydrazinium perchlorate, 4011
Hydrazinium salts, 4546
See PROPELLANTS, REDOX COMPOUNDS

HYDRAZONES $RR'C{=}NNH_2$

Glycols, Alkali hydroxides
1. Todd, D., *Org. React.*, 1948, **IV**, 8

This mixture is the Huang Minlon modification of the Wolff Kishner reaction. In the editor's experience it often leaps from the flask with sudden gas evolution. In addition to the expected nitrogen, at the operating temperature of around 200°C it is uncomfortably near the temperature of hydrogen evolution from glycol decomposition. The reduction proceeds much cooler in dimethyl sulfoxide or some of the alkoxyethanols as solvent.
See Sodium hydroxide: Glycols

HYDROGENATION CATALYSTS

1. Augustine, R. L., *Catalytic Hydrogenation*, 23, 28, London, Arnold, 1965
2. Anon., *Chem. Brit.*, 1974, **10**, 367
3. Poles, T., private comm., 1973
4. Freifelder, 1971, 74, 78, 81–83, 168, 175, 262, 263
5. Jimenez, M. H., *Org. Prep. Proced. Int.*, 1978, **10**, 295–297

DropBooks

Many hydrogenation catalysts are sufficiently active to effect rapid interaction of hydrogen and/or solvent vapour with air, causing ignition or explosion. This is particularly so where hydrogen is adsorbed on the catalyst, either before a hydrogenation (Raney cobalt, nickel, etc.), or after a hydrogenation during separation of catalyst from the reaction mixture. Exposure to air of such a catalyst should be avoided until complete purging of hydrogen with an inert gas, such as nitrogen, has been effected. With catalysts of high activity and readily reducible substrates, control of the exotherm may be required to prevent runaway reactions, particularly at high pressures [1]. A proprietary form of Raney nickel catalyst in which the finely divided metal particles are coated with a fatty amine is claimed to be free of pyrophoric hazards if it dries out [2].

Platinum-metal catalysts are preferably introduced to the reactor or hydrogenation system in the form of a water-wet paste or slurry. The latter is charged to the empty reactor: air is removed by purging with nitrogen or by several evacuations alternating with nitrogen filling: the reaction mixture is charged, after which hydrogen is admitted. The same procedure applies where it is mandatory to charge the catalyst in the dry state, but in this case the *complete* removal of air before introduction of the reaction mixture and/or hydrogen is of vital importance.

Platinum, palladium and rhodium catalysts are non-pyrophoric as normally manufactured. Iridium and, more particularly, ruthenium catalysts may exhibit

pyrophoricity in their fully reduced form, and for this reason are usually manufactured in the unreduced form and reduced in situ. Spent catalysts should be purged from hydrogen and washed free from organics with water before storage in the water-wet condition. Under no circumstances should any attempt be made to dry a spent catalyst [3].

Specialist advice on safety and other problems in the use of catalysts and associated equipment is freely available from Engelhard Industries Ltd. at Cinderford in Gloucester, where a model high-pressure hydrogenation laboratory with full safety facilities is maintained.

In a volume devoted to hydrogenation techniques and applications, there are several references to safety aspects of catalytic hydrogenation. For noble metal and nickel catalysts, low boiling solvents should be avoided to reduce the risk of ignition when catalysts are added. Risks are highest with carbon-supported catalysts, which tend to float at the air interface of the solvent. The need for dilute solutions of nitro- and polynitro-aromatics or oximes, and for relatively low concentrations of catalysts to minimise the relatively large exotherms, are stressed [4]. A simple syringe-filter apparatus is described, which permits hazard-free rinsing, near-drying and transfer of palladium black catalysts [5].

Individually indexed catalysts are:
Iridium, 4643
Lanthanum–nickel alloy, 4678
Nickel, 4820
Palladium, 4885
Platinum, 4887
Rhodium, 4892
Ruthenium, 4894
See CATALYTIC NITRO REDUCTION PROCESSES, COPPER CHROMITE CATALYST

HYDROGENATION INCIDENTS

Harak, J., *Stud. Sur. Sci. Catal.*, 1986, **27** (Catal. Hydrog.), 579–511
A comprehensive discussion of parameters and methods necessary for effective control of laboratory and industrial scale hydrogenation autoclaves, and the need for early recognition of hazardous situations is available.

For hazardous incidents involving hydrogenation,
See CATALYTIC NITRO REDUCTION PROCESSES

and the individual entries:
† Benzene, : Hydrogen, Raney nickel, 2288
Formic acid, : Palladium–carbon catalyst, 0418
† Hydrogen (Gas), : Acetylene, Ethylene, 4453
† Hydrogen (Gas), : Catalysts, Vegetable oils, 4453
† Hydrogen (Gas), : Ethylene, Nickel catalyst, 4453
† Hydrogen (Gas), : Palladium, 2-Propanol, 4453
Hydrogen peroxide, : Hydrogen, Palladium catalyst, 4477
3-Methyl-2-penten-4-yn-1-ol, 2384

1,1,1-Tris(azidomethyl)ethane, 1937
Tris(hydroxymethyl)nitromethane, 1664

See other UNIT OPERATION OR UNIT PROCESS INCIDENTS

See also CATALYTIC HYDROGENATION AUTOCLAVES

HYDROXOOXODIPEROXOCHROMATE SALTS **$M[HOCr(O_2)_2O]$**

Bailar, 1973, Vol. 3, 699

The ammonium, potassium, and thallium salts are all violently explosive. The entries are:

Ammonium hydroxooxodiperoxochromate(1−), 4230
Potassium hydroxooxodiperoxochromate(1−), 4227
Thallium hydroxooxodiperoxochromate(1−), 4228

See other PEROXOACID SALTS

HYDROXYLAMINIUM SALTS **$HON^+H_3\ Z^-$**

Anon., *Chem. Processing (Chicago)*, 1963, **26**(24), 30

Some decompositions of salts of hydroxylamine are discussed, including violent decomposition of crude chloride solutions at 140° and exothermic decomposition of the solid sulfate at 170°C. The phosphinate and nitrate decompose violently above 92 and 100°C, respectively.

Some examples are:
Hydroxylaminium chloride, 4002
Hydroxylaminium nitrate, 4524
Hydroxylaminium perchlorate, 4005
Hydroxylaminium phosphinate, 4555
Hydroxylaminium sulfate, 4575

∗ *N*-(Methylphenylphosphinoyl)hydroxylamine, 2823

See other N–O COMPOUNDS, OXOSALTS OF NITROGENOUS BASES

See Sodium nitrite

DropBooks

3-HYDROXYTRIAZENES **N=N−NOH**

Houben-Weyl, 1965, Vol. 10.3, 717

Many of the 3-hydroxytriazene derivatives produced by diazo-coupling onto *N*-alkyl or *N*-aryl hydroxylamines decompose explosively above their m.p.s. However, the heavy metal derivatives are stable and used in analytical chemistry.

See other TRIAZENES

HYPOHALITES **ROX**

1. Sidgwick, 1950, 1218
2. Chattaway, F. D., *J. Chem. Soc.*, 1923, **12** 3, 2999
3. Anbar, M. *et al.*, *Chem. Rev.*, 1954, **54**, 927
4. Lewis, D. J., private comm., 1983

This class of organic oxidant compounds, all containing O−X bonds, includes widely differing types and many compounds of limited stability. Alkyl hypochlorites, readily formed from alcohols and chlorinating agents, will explode on ignition, irradiation or contact with copper powder [1,2]. Of the many alkyl hypohalites described, only ethyl, *tert*-butyl and *tert*-pentyl are stable enough to isolate, purify and handle [3], though care is needed. Some of the lower alkyl hypochlorites are not as unstable or hazardous as was formerly thought [4]. There are the separately treated groups:

See also ACYL HYPOHALITES, BIS(FLUOROOXY)PERHALOALKANES

and the individually indexed compounds:

∗ Bromine(I) trifluoromethanesulfonate, 0312
∗ Chlorine fluorosulfate, 3975
∗ Chlorine(I) trifluoromethanesulfonate, 0320
∗ Chloroperoxytrifluoromethane, 0319
Chloryl hypofluorite, 3973
Difluoromethylene dihypofluorite
Ethyl hypochlorite, 0851
Fluorine perchlorate, 3976
Heptafluoroisopropyl hypofluorite, 1035
Heptafluoropropyl hypofluorite, 1060
Hypochlorous acid, 3995
Isopropyl hypochlorite, 1247
Methyl hypochlorite, 0434
Methyl hypofluorite, 0433
Nitryl hypochlorite, 4026
Pentafluoroselenium hypofluorite, 4368
Pentafluorosulfur hypofluorite, 4367
∗ Pentafluorosulfur peroxyhypochlorite, 3990
Pentafluorotellurium hypofluorite, 4369
∗ Perfluoro-*tert*-butyl peroxyhypofluorite, 1373
Tetrafluoroiodosyl hypofluorite, 4356
Trifluoromethyl hypofluorite, 0353

IGNITION SOURCES

1. Howard, W. B., *Chem. Eng. Progr.*, 1970, **66**(9), 59−65
2. Enstad, G., *Reconsideration of the Concept of Minimum Ignition Energy*, Euro. Fed. Chem. Engrs. Wkg. Party, March 16th 1975
3. Kashiwagi, T., *Combustion Sci. Technol.*, 1980, **21**(3−4), 131−139
4. *Guidance on RF Ignition Hazards*, GS21, HMSO, 1983
5. Anon., *Fire Prev.*, 1983, **165**, 27−31
6. Baev, V. K. *et al.*, *Chem. Abs.*, 1984, **100**, 54018
7. McMillan, A. J., *Meas. Control*, 1986, **19**(7), 41−45
8. Anon., *Fire Prev.*, 1986, (194), 45
9. Bernard, F., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 683−704, Heidelberg, ISSA, 1987

10. *Ignition of Solids*, Vlyanov, V. L., Zarko, V. E., Amsterdam, Elsevier, 1989
11. *Sources of Ignition*, Bond, J., Oxford, Butterworth-Heinemann, 1991
12. Carson, P. A. *et al., Loss Prev. Bull.*, 1992, 108
13. Carleton, F. B. *et al., Proc. Roy. Soc. London, Ser. A.*, 1994, **447**(1931), 513

Some plant incidents involving unexplained ignition sources are detailed [1]. The reason why less energetic sparks will ignite a dust cloud while more energetic sparks will not is that the latter expel dust particles from the ignition zone, while the former do not [2]. The ignition of liquid decane under high intensity CO_2 laser irradiation ($1-5$ kW/cm^2) was studied [3], as was ignition of flammable atmospheres by laser beams emergent from optical fibres for various wavelengths and targets [13]. A guide outlining the risks of RF radiation as ignition sources was published [4]. In a discussion of the principles affecting spark ignition of flammable gases and vapours, minimum ignition energies for 60 such materials are included [5]. Under certain conditions involving shock waves, hydrogen or methane released from cylinders at 20–200 bar into an air-filled chamber at 15°C/1 bar may ignite spontaneously [6].

BS 6656:1986, dealing with hazards of ignition by sparks induced by electromagnetic transmissions (radio, television, radar), is discussed in relation to the chemical, petrochemical and oil industries. For hydrogen, any transmission above 2 W radiated power is a potential ignition source [7]. An explosion in a spray drier producing powdered milk was initiated by mechanical failure of the atomiser head, rotating at 7,500 rpm and causing frictional sparks [8]. Causes of 2 cases of ignition at LPG filling stations were analysed. In one, ignition of propane occurred when filling clamps were applied to the cylinder, and in the second, ignition of butane occurred when a connecting hose burst [9]. Various aspects of the ignition of solids are covered in a recent book [10]. For an excellent summary of known causes of ignition in industry, with numerous case histories and some tables of properties [11].

DropBooks

A study of mechanisms and circumstances of spontaneous combustion with incidents and a list of susceptible materials [12]. Water is often involved.

Unexpected sources of ignition have led to many fires and explosions, usually in cases of leakage or spillage of flammable materials. Some examples are:

FRICTIONAL IGNITION OF GASES AND VAPOURS
FRICTIONAL INITIATION OF DUST CLOUDS
GRAVEL
IRRADIATION DECOMPOSITION INCIDENTS
SELF HEATING AND IGNITION INCIDENTS
Aluminium–magnesium alloy: Iron(III) oxide, Water, 0053
Aluminium–magnesium–zinc alloy, : Rusted steel, 0054
Carbon dioxide, Flammable materials, 0557
Carbon dioxide, Metals, 0557
† Ethylene, Steel-braced tyres, 0781
Oxygen (Liquid), Asphalt, 4832
† Sulfur, Static discharges, 4897

INCINERATOR DUST

See Diprotium monoxide: Incinerator dust

INDIGESTION

1. Kimura, I. *et al., Chem. Abs.*, 1993, **119**, 85759c
2. Sidebotham, G., *Chem. Phys. Processes Combust.*, 1995, 463

The afflatus of the human gut consists of carbon dioxide and hydrogen (not methane). A Japanese study of hydrogen generation as a hazard of bowel lavage solutions and a laxative is abstracted. Most produced hydrogen, especially the laxative, when incubated with dog faeces [1]. Use of nitrous oxide as an anaesthetic generates flammable gas mixtures in the intestines. Surgery with potential sources of ignition is to be avoided [2].

See Hydrogen (Gas), 4453

See also BATS

INDUCTION PERIOD INCIDENTS

In the absence of anything to prevent it, a chemical reaction will begin when the components and any necessary energy of activation are present in the reaction system. If an inhibitor (negative catalyst or chain-breaker) is present in the system, it will prevent the onset of normal reaction until the concentration of the inhibitor has been reduced by decomposition or side reactions to a sufficiently low level for reaction to begin. This delay in onset of reaction is termed the induction period.

The existence of an induction period can interfere significantly with the course of a reaction where this involves either control of the rate of reaction by regulating the rate of addition of one of the reagents, or of the reaction temperature. In the absence of reaction, the concentration of the added reagent (or the temperature) may be increased to a level at which, once reaction does begin, it may accelerate out of control and become hazardous. It is essential, therefore, in the early stages of a reaction to ensure that the desired transformation has begun, particularly if large quantities of material are involved. This may be achieved by watching for a change in colour or appearance in the reaction mixture, for an increase in the rate of heat evolution (as judged from reflux rate, need for cooling, etc.), or by removal of a sample for chemical or instrumental testing.

Grignard reagents are notorious for the existence of induction periods, and an extensive account of methods for their elimination by various activation procedures is given at the beginning of the treatise on Grignard reactions by Kharasch and Reinmuth (1954). Another long-used method of promoting the onset of reaction in on-going processes is the addition to the reaction mixture of a small quantity of reaction mixture kept from a previous batch. When organolithium reagents were made from the metal and alkyl halides, they had an even worse reputation than Grignard reagents

Some relevant examples may be found in the group entries:

ALKYL NITRATES: Lewis acids
DIALKYLZINCS
GRIGNARD REAGENTS
OXIME CARBAMATES

and in the individual entries:

† Acrylaldehyde
Aluminium tetrahydroborate, : Alkenes, Oxygen
Benzeneseleninic acid, : Hydrazine derivatives
Benzyltriethylammonium permanganate
Bis(4-hydroxyphenyl) sulfone
tert-Butyllithium, : 2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine
Calcium acetylide, : Methanol
∗ 2-Chloro-*N*-(2-hydroxyethyl)aniline
2-Cyano-4-nitrobenzenediazonium hydrogen sulfate
2,6-Dibromobenzoquinone-4-chloroimide
Dichlorine oxide
2,6-Dichlorobenzoquinone-4-chloroimide
Diethyl acetylenedicarboxylate
Dimethyl 2-chloro-4-nitrophenyl thionophosphate
Dimethyl 3-chloro-4-nitrophenyl thionophosphate
Dimethyl 4-nitrophenyl thionophosphate
N,N-Dimethyl-4-nitrosoaniline, : Acetic anhydride, Acetic acid
† Dimethyl sulfoxide
4,6-Dinitro-1,3-benzenediol
2,4-Dinitrotoluene
Fluorine, : Water
Hydrogen chloride, : Chlorine, Dinitroanilines
Hydrogen peroxide
Hydrogen peroxide, : Nitrogenous bases
Lead(IV) oxide, : Carbon black, Chlorinated paraffin
Manganese(IV) oxide
Magnesium, : Methanol
Mercury(I) azide
† Methanol, : Carbon tetrachloride, Metals
†Methyl acrylate
Nitric acid, : 1,3-Diacetoxybenzene
Nitric acid, : Formic acid
Phosphorus trichloride
Potassium dioxide
Potassium ethoxide
Sodium chlorite, : Phosphorus
Sodium dichromate, : Acetic anhydride
Sodium tetrahydroborate, : Dimethyl formamide
Succinodinitrile
† Tetracarbonylnickel, : Oxygen, Butane
2,4,6-Trichloro-1,3,5-triazine, : Dimethylformamide
2,4,6-Tris(bromoamino)-1,3,5-triazine
Zinc, : Water

DropBooks

INORGANIC ACIDS H^+

Many of the inorganic (mineral) acids have been involved in various incidents, either as catalysts or reactants, the most common, so far as frequency is concerned, being nitric acid in oxidation incidents. Individual acids are:

Amidosulfuric acid, 4499
∗ Bismuthic acid, 0228
Boric acid, 0144
Bromic acid, 0248
Chlorosulfuric acid, 3997
Chromic acid, 4229
Diamidophosphorous acid, 4547
Dioxonium hexamanganato(VII)manganate, 4553
Fluorophosphoric acid, 4297
Fluoroselenic acid, 4295
Hydriodic acid, 4423
Hydrogen azide, 4441
Hydrogen bromide, 0247
Hydrogen chloride, 3993
Hydrogen fluoride, 4294
Hydrogen hexafluorophophosphate, 4360
Iodic acid, 4424
Nitric acid, 4436
Nitrosylsulfuric acid, 4438
Nitrous acid, 4435
Orthoperiodic acid, 4542
Orthophosphoric acid, 4505
Pentafluoroorthoselenic acid, 4354
Perchloric acid, 3998
Periodic acid, 4425
Permanganic acid, 4434
Peroxomonophosphoric acid, 4506
Peroxomonosulfuric acid, 4481
Phosphinic acid, 4503
Phosphonic acid, 4504
∗ Sodium hydrogen sulfate, 4446
Sulfuric acid, 4479
Tetrafluoroboric acid, 0130
Tetraphosphoric acid, 4567

See ORGANIC ACIDS

INORGANIC AZIDES $E(N_3)_X$

1. Mellor, 1967, Vol. 8, Suppl. 2, 42
2. Evans, B. L. *et al., Chem. Rev.*, 1959, **59**, 515
3. Deb, S. K. *et al., Proc. 8th Combust. Symp.*, 1960, 289

Relationships existing between structure, stability and thermal, photochemical and explosive decomposition (sometimes spontaneous) of the inorganic azides has been extensively investigated and reviewed [1,2]. The ignition characterisitcs of explosive inorganic azides, with or without added impurities under initiation by heat or light have been discussed [3].

Relevant groups of inorganic azides are:

HALOGEN AZIDES, METAL AZIDE HALIDES,
METAL AZIDES, NON-METAL AZIDES

INORGANIC BASES OH^-

Several of the inorganic bases have been involved in various laboratory or industrial scale incidents, individual entries being:

† Ammonia, 4497
Ammonium hydroxide, 4544
Barium hydroxide, 0208
Caesium amide, 4260
Calcium carbonate, 0317
Calcium hydroxide, 3928
Calcium oxide, 3937
Lead carbonate–lead hydroxide, 0726
Lithium carbonate, 0533
Magnesium carbonate hydroxide, 0534
Magnesium oxide, 4695
Potassium carbonate, 0531
Potassium hydroxide, 4428
Sodium carbonate, 0552
Sodium hydroxide, 4445
Sodium oxide, 4802

DropBooks

INORGANIC PEROXIDES O_2^{2-}

1. Castrantas, 1970
2. Castrantas, 1965

The guide to safe handling and storage of peroxides also contains a comprehensive bibliography of detailed information [1]. The earlier publication contains tabulated data on fire and explosion hazards of inorganic peroxides [2].

See METAL PEROXIDES
PEROXOACIDS
PEROXOACID SALTS
Hydrogen peroxide, 4477

INSULATION

1. Britton, L. G., *Plant/Oper. Progr.*, 1991, **10**(3) 27
2. McDermott, P. E., *Chem. Brit.*, 1976, **12**, 69

3. Markham, H., *Chem. Brit.*, 1976, **12**, 205
4. Carrettes, G. V., *Chem. Brit.*, 1976, **12**, 204
5. Hilado, C. J., *J. Fire Flamm.*, 1974, **5**, 326–333
6. Bowes, P. C., *Fires in Oil-Soaked Lagging*, CP35/74, Garston, Building. Res. Establ., 1974
7. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 32
8. McIntosh, A. C. *et al.*, *J. Chem. Soc., Faraday Trans.*, 1996, **92**(16), 2965

The porous and absorbent materials commonly used to lag industrial reactors may present active surfaces for the reaction of leaked contents with themselves or air. Resultant hotspots or fires can have devastating consequences, especially when endothermic materials are within. A study of exotherm and autoignition (from start temperatures as low as 65°C) of several polyamines, glycols, olamines and other compounds is detailed, together with an empirical method for predicting hazards from flash points and autoignition temperatures [1]. In these circumstances the temperature of ignition is often well below the conventionally determined AIT. Experiments showed an ignition temperature some 100–200°C below the AIT, depending on the nature of the oils and of the lagging material into which they were soaked [2]. The experimental technique was criticised on the grounds that excess air is supplied to the sample, whereas in practice access of air is often severely limited. An alternative procedure to simulate practice more closely is described, and the results for leakage of heat-transfer oils are given, ignition generally occurring at 160–200°C. The need for care to avoid fire when removing oil-contaminated lagging is stressed [3].

Attention was drawn to the existing test for the self-heating properties of textile oils, and the promoting (co-oxidant) effect of iron or copper in reducing the AIT of the oils [4]. The presence of combustibles incorporated into lagging materials during manufacture can give rise to significant self-heating effects in uncontaminated lagging [5]. The theoretical background and current experimental progress were reviewed [6]. Two incidents involving ignition of PCB heat transfer oil on calcium silicate lagging were reported. Foamed glass lagging appears to be advantageous for high-risk areas [7]. A computer model of lagging fire ignition has been developed [8].

See Ethylene oxide
See also PACKAGING INCIDENTS

INTERHALOGENS

Kirk-Othmer, 1966, Vol. 9, 585–598

The fluorine-containing members of this group are oxidants almost as powerful as fluorine itself. Individually indexed compounds are:

Bromine fluoride, 0238
Bromine pentafluoride, 0243
Bromine trifluoride, 0241
Chlorine fluoride, 3971
Chlorine pentafluoride, 3989
Chlorine trifluoride, 3981

Iodine bromide, 0254
Iodine chloride, 4013
Iodine heptafluoride, 4378
Iodine pentafluoride, 4355
Iodine trichloride, 4139

IODINE COMPOUNDS

Several iodine compounds are explosively unstable, individually indexed compounds being:

3-Acetoxy-4-iodo-3,7,7-trimethylbicyclo[4.1.0]heptane, 3544
Ammonium iodate, 4513
Ammonium periodate, 4514
Azidoiodoiodonium hexafluoroantimonate, 4361
[*I,I*-Bis(trifluoroacetoxy)iodo]benzene, 3239
Boron triiodide, 0150
4-*tert*-Butyliodylbenzene, 3319
Caesium tetraperchloratoiodate, 4161
Calcium 2-iodylbenzoate, 3625
Dicyanoiodonium triflate, 1048
Diiodamine, 4426
1,2-Diiodobenzene, 2172
3,5-Dimethyl-4-[*I,I*-bis(trifluoroacetoxy)iodo]isoxazole, 3115
∗ 2-Ethoxy-1-iodo-3-butene, 2449
Hexamethylenetetramine tetraiodide, 2471
(Hydroxy)(oxo)(phenyl)-λ^3-iodanium perchlorate, 2299
Iodinated poly(sulfur nitride), 4622
Iodic acid, 4424
Iodine azide, 4621
Iodine bromide, 0254
Iodine chloride, 4013
Iodine dioxide trifluoride, 4334
Iodine heptafluoride, 4378
∗ Iodine isocyanate, 0524
Iodine(V) oxide, 4627
Iodine(VII) oxide, 4628
Iodine pentafluoride, 4355
Iodine(III) perchlorate, 4140
Iodine triacetate, 2394
Iodobenzene, 2249
4-Iodo-3,5-dimethylisoxazole, 1868
Iododisilane, 4543
2(2-Iodoethyl)-1,3-dioxolane, 1928
1-Iodohexa-2,4-diene, 2393
3-Iodo-4-methoxy-4,7,7-trimethylbicyclo[4.1.0]heptane, 3412
† 2-Iodopropane, 1252

DropBooks

† 3-Iodopropene, 1174
2-Iodosovinyl chloride, 0691
Iodosylbenzene, 2252
Iodosylbenzene tetrafluoroborate, 2295
4-Iodosyltoluene, 2753
4-Iodotoluene, 2750
† Iodotrimethylsilane, 1306
4-Iodylanisole, 2755
Iodylbenzene, 2253
2-Iodylbenzoic acid, 2681
4-Iodyltoluene, 2754
2-Iodylvinyl chloride, 0692
Nitrogen triodide, 4633
Nitrogen triiodide–ammonia, 4635
Nitrogen triiodide–silver amide, 4634
μ-OxO-*I,I*-bis(trifluoroacetato-*O*)-*I,I*-diphenyliodine (III), 3698
Oxybisphenyliodonium bistetrafluoroborate, 3475
Orthoperiodic acid, 4542
Pentafluoroiodosylbenzene, 2058
Periodic acid, 4425
9-Phenyl-9-iodafluorene, 3747
Phenyliodine(III) chromate, 2247
Phenyliodine(III) nitrate, 2251
Phenyl, phenylethynyliodonium perchlorate, 3635
I-Phenyl-*I*-(*p*-toluenesulfonyloxy)-(2-azido-2-phenyl)vinyliodine(III)
Phosphorus triiodide, 4636
Poly(dimercuryimmonium iodide hydrate), 4455
Potassium iodate, 4619
Potassium periodate, 4620
Sodium iodate, 4624
Tetrafluoroiodosyl hypofluorite, 4356
Tetraiodoarsonium tetrachloroaluminate, 0057
Tetraiododiphosphane, 4637
Tetraiodoethylene, 0986
1,1,1-Triacetoxy-1,2-benziodoxol-3-one, 3610
Trifluoroacetyliminoiodobenzene, 2903
Trifluoromethyliodine(III) isocyanate, 1045
Triiodocyclopropenium iodide, 1339

vic-IODO-ALKOXY or -ACETOXY COMPOUNDS −C(I)−C(OR)− or −C(I)−C(OAc)−

Dimmel, D. R., *Chem. Eng. News*, 1977, **55**(27), 38

Treatment of 3,7,7-trimethylbicyclo[4.1.0]heptane (Δ3-carene) with iodine and copper acetate in methanol gave 3-iodo-4-methoxy-4,7,7-trimethylbicyclo[4.1.0] heptane. A 50 g sample exploded violently after standing at ambient temperature in a closed container for 10 days. This and the corresponding iodoacetoxy

compound showed large exotherms at 90°C on DTA examination, ΔH for the latter substance being calculated as 4.19 MJ/mol (13.1 kJ/g). Similar products derived from methylcyclohexene also exhibited substantial exotherms from 60°C upwards. It is recommended that *vicinal* iodo-alkoxy or -acetoxy derivatives of terpenes should be handled very cautiously.

See IODINE COMPOUNDS

ION EXCHANGE RESINS

Ammonia solution

Colman, C., *Chem. Engrg.* (New York), 1980, **87**, 274

Passage of a conc. solution of ammonia through a column of the acid form of a cation exchange resin led to a sudden neutralisation exotherm which damaged the bed, owing to its poor heat dissipation characteristics.

Dichloromethane

See Dichloromethane: Azide form of quaternary etc.

Dichromates

1. Earle, H., *Chem. & Ind.*, 1979, 391
2. Ardern, T. V., *Chem. & Ind.*, 1972, 532

The possibility is discussed of cleaning organically fouled ion exchange resins by treatment with weakly acid dichromate solutions [1]. The dangers of using separate dichromate treatment (which produces very high loading on the resin), and then mineral acid treatment, which liberates very high concentrations of chromic acid and leads to violent or explosive oxidation of the organic material (or of the resin), are stressed [2].

See Nitric acid: Ion exchange resins

DropBooks

Sugar solution

Colman, C., *Chem. Engrg.* (New York), 1980, **87**, 224

When passage of a sugar solution at 90°C through a weak-base anion exchange resin was interrupted, an explosion occurred. This was attributed to an exothermic Maillard reaction (interaction of an amino acid with a glycosidic OH group) under the poor heat transfer conditions in a particulate bed without fluid flow.

Water

1. Anon., *Chem. Eng. News*, 1953, **31**, 5120
2. Anon., *Chem. Eng. News*, 1948, **26**, 1480
3. *MCA Case History No. 2155*

A three-year-old sample of ion exchange resin was soaked in dilute hydrochloric acid, and then charged into a 2.5 cm diameter glass column. After soaking in distilled water for 15 min, the tube burst violently, presumably owing to swelling of the resin. Process resins as far as possible before charging into a column [1]. The earlier incident involved a column, charged with dry resin, which burst when

wetted [2]. The case history involved dry resin which expanded and split a glass column when wetted with an aqueous salt solution.

IRRADIATION DECOMPOSITION INCIDENTS

Several instances are recorded where the energy of activation needed to initiate decomposition of various (usually unstable) materials has been provided by radiation of various types. Such incidents may be found under the group entries:

CHLOROPHYLL
DIOXYGENYL POLYFLUOROSALTS
IGNITION SOURCES
INORGANIC AZIDES

and in the individual entries:

Azidoacetic acid, 0774
Benzoyl nitrate, 2689
Bis(cyclopentadienyldinitrosylchromium), 3275
∗ Bis(methylcyclopentadienyl)peroxoniobium chloride, 3522
Borazine, 0176
Caesium pentafluorotelluramide, 4257
Caesium tetraperchloratoiodate, 4161
∗ Calcium hypochlorite, 3924
† Carbon disulfide, 0560
Carbonic diazide, 0550
Chlorine dioxide, 4042
Dicyclopentadienylperoxyniobium chloride, 3271
Difluorodiazirine, 0342
1,8-Diphenyloctatetrayne, 3788
Glyceryl trinitrate, 1196
Hexaoxygen difluoride, 4327
Iodine(III) perchlorate, 4140
1-Iodo-1,3-butadiyne, 1381
Isopropyl hypochlorite, 1247
Mercury(I) cyanamide, 0523
Nitrogen (Liquid), 4735
Nitrogen trichloride, 4143
Plutonium(IV) nitrate, 4768
Potassium perchlorate, 4018
Potassium triazidocobaltate(1−), 4212
Radon, : Water, 4893
∗ Silver acetylide–silver nitrate, 0569
Silver azide, 0023
Trifluoromethyl hypofluorite, : Hydrocarbons, 0353

ISOCYANIDES RN=C:

Acids
Sidgwick, 1950, 673
Acid catalysed hydrolysis of isocyanides (‘carbylamines’) to primary amines and formic acid is very rapid, sometimes explosively so.
See DIISOCYANIDE LIGANDS

ISOPROPYLIDENE COMPOUNDS $Me_2C=C$

Ozone
See Ozone: Isopropylidene compounds

ISOXAZOLES

Cardillo, P., *Chim. e Ind.* (Milan), 1988, **70**(6), 90–91
After an incident involving the violent decomposition of hot 3-methyl-5-amino-isoxazole, the thermal stability of 7 other isoxazole derivatives was studied by DSC, TGA and ARC. Only 4-amino-3-isoxazolidinone decomposed exothermally in an open crucible, but all did so in sealed capsules, evolving much gas. The results below give isoxazole derivative, ARC onset temperature of decomposition (°C)/adiabatic exotherm (°C)/max. pressure (bar); and DSC heat of decomposition (kJ/g), respectively for all 9 compounds.

Isoxazole, 136/611/23, 1.36; 5-methyl-, 171/535/10, 1.08; 3,5-dimethyl-, 210/687/17, 3-amino-, 115/791/19, 2.67; 3-carbonamido-5-methyl-, 155/792/11, 1.22; 3-amino-5-methyl-, 140/77/above 170 (vent), 1.97; 5-amino-3-methyl-, 90/650/above 170 (vent), 1.43; 4-amino-3-isoxazolidinone, 76/647/11, 1.67; 3-phenyl-5-isoxazolone, 105°/659°/9 bar, 0.985 kJ/g.

DrOpBOOKS

Individual entries are :
3-Aminoisoxazole, 1136
5-Aminoisoxazole-3-carbonamide, 1476
4-Amino-3-isoxazolidinone, 1137
3-Amino-5-methylisoxazole, 1501
5-Amino-3-methylisoxazole, 1502
3,5-Dimethylisoxazole, 1888
† Isoxazole, 1110
5-Methylisoxazole, 1468
3-Phenyl-5-isoxazolone, 3122
See other GAS EVOLUTION INCIDENTS, N–O COMPOUNDS

JOJOBA WAX (Esters of C_{20-22} monoene acids and alcohols)

Ozone
Zabicky, J. *et al., J. Am. Oil Chem. Soc.*, 1986, **63**, 1547–1550

The solid diozonide prepared from jojoba wax decomposed violently at 110–120°C
See other OZONIDES

KETONE PEROXIDES

1. Davies, 1961, 72
2. Kirk-Othmer, 1967, Vol. 14, 777

The variety of peroxides (monomeric, dimeric, trimeric or polymeric) which can be produced from interaction of a given ketone and hydrogen peroxide is very wide (see type groups below for structures). The proportions of the products in the reaction mixture depend on the reaction conditions used as well as the structure of the ketone. Many of the products appear to coexist in equilibrium, and several types of structure are explosive and sensitive in varying degrees to heat and shock. Extreme caution is therefore required in handling ketone peroxides in high concentrations, particularly those derived from ketones of low MW. Acetone is thus entirely unsuitable as a reaction or cleaning solvent whenever hydrogen peroxide is used [1,2]. Relevant groups are:

CYCLIC PEROXIDES
1-OXYPEROXY COMPOUNDS
POLYPEROXIDES

Individually indexed compounds are:

Bis(2-hydroperoxy-2-butyl) peroxide, 3078
3,6-Diethyl-3,6-dimethyl-1,2,4,5-tetraoxane, 3052
3,6-Di(spirocyclohexane)-1,2,4,5-tetraoxane, 3546
3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexoxonane, 3195
3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane, 2517
3,6,9-Triethyl-3,6,9-trimethyl-1,2,4,5,7,8-hexoxonane, 3562
Tri(spirocyclopentane)1,1,4,4,7,7-hexoxonane, 3693

KETOXIMINOSILANES **$RSi(ON{=}CMeEt)_3$**

Tyler, L. J., *Chem. Eng. News*, 1974, **52**(35), 3

During preparation of tris(ketoximino)silanes, two violent explosions attributed to acid-catalysed exothermic rearrangement/decomposition reactions occurred. Although these silane derivatives can be distilled under reduced pressure, the presence of acidic impurities (e.g. 2-butanone oxime hydrochloride, produced during silane preparation) drastically reduces thermal stability. Iron(III) chloride at 500 ppm caused degradation to occur at 150°, and at 2% concentration violent decomposition set in at 50°C.

See 2-Butanone oxime hydrochloride
See other OXIMES

KINETICS AND INSTABILITY

Grewer, T., *DECHEMA Monograph*, 1980, 88(1818–1835), 21–30

One of the principal causes of batch chemical processes becoming unstable is the combination of a high reaction exotherm and a low reaction rate (or rates if there is more than one component reaction in the overall process). A secondary cause of reaction delay leading to instability is too little mass transfer. To permit safe operation of such reaction systems, the reaction energy (which may be expressed as a dimensionless reaction number) and the reaction rate(s) must be known. The possibility of there being a lower safe limit as well an upper safe limit to reaction temperature is discussed.

KJELDAHL METHOD

1. Beet, A. E., *J. R. Inst. Chem.*, 1955, **79**, 163, 269
2. McDonald, M. S., *Lab. Pract.*, 1979, **28**, 927
3. Pick, R.'W., Internet, 1996

Possible hazards introduced by variations in experimental techniques in Kjeldahl nitrogen determination were discussed [1]. Modern variations involving use of improved catalysts and hydrogen peroxide to increase reaction rates, and of automated methods, have considerably improved safety aspects [2]. An anecdote is given of the classic technique when sodium hydroxide was to be added to the sulphuric acid digestion and was allowed to trickle down the wall of the flask. It layered over the sulphuric acid. Gentle mixing then provoked rapid reaction and a steam explosion [3].

DropBooks

KRYPTON COMPOUNDS

Very few are known, all may be seen as derived from FKr^+. All are thermodynamically unstable and energetic fluorinating agents. Listed are:

Fluorohydrocyanokrypton hexafluoroarsenate, 0367

Fluorokrypton hexafluoroarsenate, 0096

Krypton difluoride, 4313

See also XENON COMPOUNDS

LAGGING

See INSULATION

LANTHANIDE IODIDE SILICIDES MISi

Mattausch, H. *et al., Angew. Chem. (Int.)*, 1998, **37**(4), 499

The MISi compounds of Lanthanum, Cerium and Praseodymium, and two slightly less iodinated lanthanum derivatives were prepared by fusing stoichiometric mixtures of the triiodides, the metal and silicon. They ignite violently on contact with water.

LANTHANIDE METAL NITROBENZOATES $M(OCO.C_6H_4NO_2)_3$

See Lanthanum 2-nitrobenzoate
Scandium 3-nitrobenzoate, 3816
Yttrium 4-nitrobenzoate, 3817
See other HEAVY METAL DERIVATIVES, NITROARYL COMPOUNDS

LANTHANIDE METALS

Oxidants
Bailar, 1973, Vol. 4, 70
While there are considerable variations in reactivity, several of the series of lanthanide metals ignite in halogens above 200°, in air or oxygen above 150–180°C, or lower in presence of moisture.
See Europium
See other METALS

LANTHANIDE–TRANSITION METAL ALLOY HYDRIDES

$LaNi_5H_6$, $LaNi_{4.5}Al_{0.5}H_5$

Imamoto, T. *et al., J. Org. Chem.*, 1987, **52**, 5695
Several lanthanide–transition metal alloys ($LaNi_5$, $PrCo_5$, $SmCo_5$) readily absorb large volumes of hydrogen under mild conditions, and some of these alloy hydrides function as active hydrogenation catalysts: e.g., the title structures, which are pyrophoric in air. Analogous hydrides may be expected to behave similarly.
See HYDROGENATION CATALYSTS, PYROPHORIC MATERIALS

LASSAIGNE TEST

1. Lance, R. C. *et al., Microchem. J.*, 1975, **20**, 103–110
2. Taylor, D. A. H., *Chem. Brit.*, 1978, **14**, 70
3. Mumford, C., *Chem. Brit.*, 1978, **14**, 170
4. Ingham, P. L., *Chem. Brit.*, 1978, **14**, 326
5. Sugden, T. M. *et al., Chem. Brit.*, 1978, **14**, 326
6. Turfitt, G. E., *Chem. Brit.*, 1979, **15**, 614
7. McCulloch, A., *Chem. Brit.*, 1979, **15**, 614
8. Boulton, L. H., *Educ. Chem.*, 1973, **10**, 231
9. Guthrie, R. D. *et al., Chem. Brit.*, 1979, **15**, 614
10. Mazor, L., *Acta Chim. Acad. Sci. Hung.*, 1979, **101**, 3–6

Correspondence on safety aspects of the Lassaigne sodium fusion test [1]–[3] included a description of the use of 3 mm lengths of 2 mm sodium wire (from an enlarged die) as a convenient source of small pieces of sodium [4]. Subsequently the safer characteristics of zinc–calcium hydroxide [5], or zinc–sodium carbonate [6] fusion methods were propounded, though these methods may not always work with volatile fluoro compounds [7]. Overall advantage is claimed, however, for an oxygen combustion technique [8], using a flask fitted with a pressure-relieving (Bunsen) valve [9]. A safe development for organic compounds containing the

hetero elements S, P, As, halogens and/or metals is to fuse the compound with potassium in vacuo at 300–500°C. After treating the cooled melt with ethanol and then water, normal microanalytical detection of ions can be used [10].

LEAD SALTS OF NITRO COMPOUNDS

Fogel'zang, A. E. *et al.*, *Chem. Abs.*, 1978, **88**, 63813

The lead salts of nitromethane, mono-, di- or tri-nitrophenols burn at faster rates (up to 640-fold) than the parent compounds. Lead salts of trinitromethane, trinitrobutyric acid or dinitro-benzoic or -p-toluic acids burn at slightly faster rates (up to 10-fold) than the parent compounds.

See other HEAVY METAL DERIVATIVES

LECTURE DEMONSTRATIONS

1. Bodner, C. M., *J. Chem. Educ.*, 1985, **62**(12), 1105–1107
2. Schibeci, R. A., *Educ. Chem.*, 1988, **25**(5), 150–153

A variety of chemical lecture demonstrations involving unstable or highly reactive materials which have led to accidents are reviewed, and practical suggestions made to avoid such incidents [1]. Safety aspects are discussed and some relevant books and articles reviewed [2].

LIGHT ALLOYS

Anon., *Fire Prot. Assoc. J.*, 1959, (44), 28

DropBooks

Experiments to determine the probability of ignition of gas or vapour by incendive sparks arising from impact of aluminium-, magnesium- and zinc-containing alloys with rusty steel are described. The risk is greatest with magnesium alloys, where the higher the magnesium content, the lower the impact energy necessary for incendive sparking. Wide ranges of ignitable gas concentrations (flammability limits) also tend to promote ignition.

See Iron(III) oxide: Aluminium and subsequent entries
Magnesium Metal oxides, 4403

See also THERMITE REACTIONS

LIME FUSION

See Calcium hydroxide: Polychlorinated phenols, etc.

LINSEED OIL

FPA H90, 1980

1. Watts, B. G., private comm., 1965
2. Taradoire, F., *Rev. Prod. Chim.*, 1925, **28**, 114–115

Cloths used to apply linseed oil to laboratory benches were not burned as directed, but dropped into a waste bin. A fire developed during a few hours and destroyed

the laboratory. Tests showed that heating and ignition were rapid if a draught of warm air impinged on the oil-soaked cloth. Many other incidents involving ignition of autoxidisable materials dispersed on absorbent combustible fibrous materials have been recorded [1]. Practical tests on the spontaneous combustion of cotton waste soaked in linseed oil and other paint materials had been reported 40 years previously [2].

See also INSULATION

LIQUEFIED GASES

Water

1. Urano, Y. *et al., Chem. Abs.*, 1976, **84**, 107979; 1977, 86, 108970
2. Porteous, W. M. *et al., Chem. Eng. Progr.*, 1976, **72**(5), 83–89
3. Fowles, G. R., *Science*, 1979, **204**, 168–169
4. Hixson, R. S., *Diss. Abstr. Int.*, 1981, **B41**, 3070–3078
5. Flock, R. A. *et al., Proc. Amer. Phys. Soc. Top. Conf.: Shock Waves in Condensed Matter*, 1984, 273–276

The explosive phenomena produced by contact of liquefied gases with water were studied. Chlorodifluoromethane produced explosions when the liquid–water temperature differential exceeded 92°C, and propene did so at differentials of 96–109°C. Liquid propane did, but ethylene did not, produce explosions under the conditions studied [1]. The previous literature on superheated vapour explosions has been critically reviewed, and new experimental work shows the phenomenon to be more widespread than had been thought previously. The explosions may be quite violent, and mixtures of liquefied gases may produce overpressures above 7 bar [2]. Alternative explanations involve detonation driven by phase changes [3,4] and do not involve chemical reactions. Explosive phase transitions from superheated liquid to vapour have also been induced in chlorodifluoromethane by 1.0 J pulsed ruby laser irradiation. Metastable superheated states (of 25°C) achieved lasted some 50 ms, the expected detonation pressure being 4–5 bar [5].

See LIQUEFIED NATURAL GAS, SUPERHEATED LIQUIDS, VAPOUR EXPLOSIONS

LIQUEFIED NATURAL GAS

FPA H30, 1974

Organic liquids, or Water

1. Katz, D. L. *et al., Hydrocarbon Proc.*, 1971, **50**, 240
2. Anon., *Chem. Eng. News*, 1972, **50**(8), 57
3. Yang, K., *Nature*, 1973, **243**, 221–222
4. *NFPA 59A*, Quincy (Ma), Natl. Fire Prot. Assocn., 1985

The quite loud ‘explosions’ (either immediate or delayed) which occur when LNG (containing usually high proportions of heavier materials) is spilled onto water are non-combustive and harmless [1]. Superheating and shock-wave phenomena are involved [2]. There is a similar effect when LNG of normal composition (90% methane) is spilled on to some C_5C_8hydrocarbons or methanol, acetone or

2-butanone [3]. A recent US National Fire Code covers site selection, design, construction and fire prevention aspects of LNG installations [4].

See SUPERHEATED LIQUIDS

LIQUEFIED PETROLEUM GASES

1. Various authors, *J. Haz. Mat.*, 1988, **20**, 3–62
2. Anon., *Loss Prev. Bull.*, 1987, (77)
3. *NFPA 58, 59, 59A*, Quincy (Ma), Natl. Fire Prot. Assocn., 1989, 1989, 1985, resp.
4. *Institute of Petroleum Model Code of Safe Practice*, Vol. 1, New York, Wiley, 1987
5. *The Storage of LPG at Fixed Installations*, Health and Safety Executive (UK), 1987
6. *The Keeping of LPG in Cylinders and Similar Containers*, Guidance Note CS4, Health and Safety Executive (UK), 1986
7. *Safe Handling of LPG* (2 videos), Inst. Chem. Eng. Rugby (UK).

Complete issues are devoted to various aspects of the fire and explosion hazards associated with bulk storage and transportation of liquefied petroleum gases, including fire exposure tests, simulation and prediction of various effects with computer programs, and preventive measures [1] and actual incidents [2]. Users should consult statutory requirements and codes of practice[3,4,5,6]. A video training package is available [7]

See also CRYOGENIC LIQUIDS, LIQUEFIED GASES, LIQUEFIED NATURAL GAS

DropBooks

LIQUID AIR

Liquid air, formerly used widely as a laboratory or industrial cryogenic liquid, has been involved in many violent incidents. Many of these have involved the increased content of residual liquid oxygen produced by fractional evaporation of liquid air during storage. However, liquid air (with ~30 vol% oxygen content) is still a powerful oxidant in its own right. Liquid nitrogen, now widely available, is recommended as a safer coolant than liquid air, though care is still necessary to prevent condensation of atmospheric oxygen during its use.

Carbon disulfide

Biltz, W., *Chem. Ztg.*, 1925, **49**, 1001

A mixture prepared as a cooling bath exploded violently and apparently spontaneously.

Charcoal

Taylor, J., *J. Sci. Instrum.*, 1928, **5**, 24

Accidental contact via a cracked glass trap caused a violent explosion. Nitrogen is a safer coolant.

Ether

Danckwort, P. W., *Angew. Chem.*, 1927, **40**, 1317

Addition of liquid air to ether in a dish caused a violent explosion after a short delay. Previous demonstrations had been uneventful, though it was known that such mixtures were impact- and friction-sensitive.

Hydrocarbons

McCartey, L. V. *et al., Chem. Eng. News*, 1949, **27**, 2612

All hydrocarbons (and most reducing agents) form explosive mixtures with liquid air.

See Nitrogen (Liquid)
Oxygen (Liquid), 4832

LITHIUM PERALKYLURANATES **$Li[UR_n]$**

Sigurdson, E. R. *et al., J. Chem. Soc., Dalton Trans.*, 1977, 818

In a series of solvated lithium peralkyluranate(IV) and (V) complexes, all were pyrophoric and the former type may explode unpredictably at ambient temperature.

See related ALKYLMETALS

See other HEAVY METAL DERIVATIVES, PYROPHORIC MATERIALS

LUBRICANTS

Several incidents involving reaction of various oxidants with lubricants used in or on moving parts of chemical plant have occurred, and this possibility should be guarded against when oxidants are to be used in equipment with lubricated parts. Some incidents may be found under the entries:

Bromine trifluoride: Silicone grease, 0241
Chlorine: Silicones, 4047
Dinitrogen tetraoxide: Laboratory grease, 4747
Nitric acid: Silicone oil, 4436
Oxygen (Gas): Oil films, 4831
Sodium bromate: Grease, 0257

LYCOPODIUM POWDER

Kubala, T. A. *et al., Chem. Abs.*, 1982, **96**, 145450

In a study of discharge ignition of air suspensions of the powder, it was found that the wall layers deposited from air dispersions were as easily ignited as the dispersions.

See DUST EXPLOSION INCIDENTS (references 25, 29)

MAGNETIC STIRRERS

(Editor's opinion)

The magnetic stirrer hotplates now commonly used, whereby a follower on the bottom of the reaction vessel is impelled by an electric motor beneath, are not very

effective. They do not disperse explosive solids, liquids, or mixtures very well, usually leaving an annulus at the bottom. They do, however, grind this against the wall, especially when restarted after removal of the flask. Several explosions in this book seem likely to have been initiated thus. An overhead stirrer, which does not permit grinding between surfaces, is to be preferred, and generally mixes better too. Contrary to some recommendations, the magnetic stirrer is not a way to avoid ignition by sparking electric motors; it includes one and most flammable vapours are denser than air, settling downwards and not up. Probably the safest laboratory agitator is an overhead air-turbine motor, especially if run on nitrogen.

MAXIMUM REACTION HEAT

Yoshida, T., *Handbook of Hazardous Reactions with Chemicals*, Tokyo, Tokyo Fire Dept., 1980

The calculated figures for maximum reaction heat which are given throughout this text for various reactive pairs of chemicals are quoted from the extensive tables given in the above book. The figures indicate the heat release that could occur in 1 g of a binary mixture at the composition calculated to give the maximum, with the heat release in kJ and the composition in wt% of the compound against which the MRH figure is given. Most values are given in the form MRH 2.45/66, indicating that the maximum reaction heat of 2.45 kJ/g is developed for a mixture containing 66% of the component A against which the figure is quoted. In some instances the values are in the form 2.45/99+ or 2.45/tr. In the former case this implies that the component A is decomposed catalytically by traces of the other component B, and in the latter case that traces of the component A catalyse decomposition of the other component B.

DropBooks

The book also gives a rating of probability of ignition for each reactive pair, based on whether the energy release is above 2.9 kJ/g (Grade A, high probability), between 1.25 and 2.9 (B, medium probability), between 0.42 and 1.25 (C, low probability) or below 0.42 kJ (D, nil). Nearly 400 pages of tables of binary mixtures are given in the book, but only the figures for binary mixtures already in this Handbook for other reasons have been inserted, to permit a rough correlation to be made between the calculated figures for energy release and the physical effects in the incidents described.

MERCURY COMPOUNDS

A number of mercury compounds show explosive instability or reactivity in various degrees, including the group:

See also POLY(DIMERCURYIMMONIUM) COMPOUNDS

and the individually indexed compounds:

- ∗ Acetoxydimercurio(perchloratodimercurio)ethenone, 1413
- ∗ Acetoxymercurio(perchloratomercurio)ethenone, 1412

Allylmercury(II) iodide, 1173

N,N-Bis(bromomercurio)hydrazine, 0268

N,N′-Bis(chloromercurio)hydrazine, 4064

* μ-1,2-Bis(cyanomercurio)ethanediylidenedimercury(II), 1798
* Bis(dimethylarsinyldiazomethyl)mercury, 2467
Bis(ethoxycarbonyldiazomethyl)mercury, 2978
1,2-Bis(hydroxomercurio)-1,1,2,2-bis(oxydimercurio)ethane, 0708
Bis-*N*(imidosulfurdifluoridato)mercury, 4342
* Bis(trimethylsilyl)mercury, 2593
Chloratomercurio(formyl)methylenemercury(II), 0654
Chloromercuriodiphenylgold, 3473
* Di[bis(trifluoromethyl)phosphido]mercury, 1375
Diisopentylmercury, 3368
* Dimercury dicyanide oxide, 0983
Dimethylmercury, 0907
Diphenylmercury, 3480
Dipropylmercury, 2537
2-Hydroxyethylmercury(II) nitrate, 0857
Mercury(II) acetylide, 0975
Mercury(II) amide chloride, 3999
Mercury(I) azide, 4612
Mercury(II) azide, 4604
Mercury 5,5′-azotetrazolide, 0980
Mercury bis(chloroacetylide), 1356
Mercury(I) bromate, 0271
Mercury(II) bromate, 0270
Mercury(II) bromide, 0269
Mercury(I) chlorite, 4080
Mercury(II) chlorite, 4077
Mercury(I) cyanamide, 0523
* Mercury(II) cyanate, 0977
Mercury(II) cyanide, 0976
Mercury(II) *aci*-dinitromethanide, 0707
Mercury(I) fluoride, 4312
Mercury(II) formohydroxamate, 0804
Mercury(II) fulminate, 0978
Mercury(I) hypophosphate, 4617
Mercury(II) iodide, 4602
Mercury(I) nitrate, 4609
Mercury(II) nitrate, 4603
Mercury nitride, 4615
Mercury(II) 5-nitrotetrazolide, 0981
Mercury(II) oxalate, 0982
‘Mercury(I) oxide’, 4613
Mercury(II) oxide, 4605
Mercury(II) *N*-perchlorylbenzylamide, 3651
Mercury peroxide, 4606
Mercury(II) peroxybenzoate, 3637
Mercury(II) picrate, 3433

Mercury(II) sulfide, 4607
∗ Mercury(II) thiocyanate, 0979
Mercury(I) thionitrosylate, 4610
2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane, 1592
2-Naphthalenediazonium trichloromercurate, 3248
Poly(diazomethylenemercury), 0522
Poly(dimercuryimmonium hydroxide), 4422
Potassium tetracyanomercurate(II), 1797
Sodium 2-hydroxymercurio-4-*aci*-nitro-2,5-cyclohexadienonide, 2171
Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,
5-cyclohexadienonide, 2111
Tetra(3-aminopropanethiolato)trimercury perchlorate, 3582
Tetrakis(hydroxymercurio)methane, 0471
Trimercury tetraphosphide, 4616
∗ Tris(iodomercurio)phosphine, 4614

METAL ABIETATES

Anon., *Fire Prot. Assoc. J.*, 1958, 255

Aluminium, calcium, cobalt, lead, manganese, sodium and zinc abietates ('resinates'), when finely divided are subject to spontaneous heating and ignition. Store in sealed metal containers away from fire hazards.

Individually indexed compounds are:
Aluminium abietate, 3917
Calcium abietate, 3900
Lead abietate, 3902
Manganese abietate, 3901
Sodium abietate, 3805
Zinc abietate, 3903
See other SELF-HEATING AND IGNITION INCIDENTS

DropBooks

METAL ACETYLIDES **C≡CM**

1. Brameld, V. F. *et al., J. Soc. Chem. Ind.*, 1947, **66**, 346
2. Houben-Weyl, 1970, Vol. 13.1, 739
3. Rutledge, 1968, 85–86
4. Miller, 1965, Vol. 1, 486
5. Dolgopolskii, I. M. *et al., Chem. Abs.*, 1947, **41**, 6721
6. Roger, E. C. *et al., Inorg. Chim. Acta*, 1984, **90**(3), L47–L49
7. Köhn, J., *Chem. Abs.*, 1986, **104**, 212405

Previous literature on formation of various types of copper acetylides is discussed and the mechanism of their formation is examined, with experimental detail. Whenever a copper or copper-rich alloy is likely to come into contact with atmospheres containing [1] ammonia, water vapour and acetylene, or [2] lime-sludge, water vapour and acetylene, or a combination of these two, there is the probability of acetylide formation and danger of explosion. The action is aided by the presence

of air, or air with carbon dioxide, and hindered by the presence of nitrogen. Explosive acetylides may be formed on copper or brasses containing more than 50% copper when these are exposed to acetylene atmospheres. The acetylides produced by action of acetylene on ammoniacal or alkaline solutions of copper(II) salts are more explosive than those from the corresponding copper(I) salts [1]. The hydrated forms are less explosive than the anhydrous material [2].

Catalytic forms of copper, mercury and silver acetylides, supported on alumina, carbon or silica and used for polymerisation of alkanes, are relatively stable [3]. In contact with acetylene, silver and mercury salts will also give explosive acetylides, the mercury derivatives being complex [4]. Many of the metal acetylides react violently with oxidants. Impact sensitivities of the dry copper derivatives of acetylene, buten-3-yne and 1,3-hexadien-5-yne were determined as 2.4, 2.4 and 4.0 kg m, respectively. The copper derivative of a polyacetylene mixture generated by low-temperature polymerisation of acetylene detonated under 1.2 kg m impact. Sensitivities were much lower for the moist compounds [5]. Explosive copper and silver derivatives give non-explosive complexes with trimethyl-, tributyl- or triphenyl-phosphine [6]. Formation of silver acetylide on silver-containing solders needs higher acetylene and ammonia concentrations than for formation of copper acetylide. Acetylides are always formed on brass and copper or on silver-containing solders in an atmosphere of acetylene derived from calcium carbide (and which contains traces of phosphine). Silver acetylide is a more efficient explosion initiator than copper acetylide [7].

Individually indexed compounds in this often dangerously explosive class are:

* Acetylenebis(triethyllead), 3672
* Acetylenebis(triethyltin), 3674

Barium acetylide, 0575

* Bis(dimethylthallium)acetylide, 2519

3-Buten-1-ynyldiethylaluminium, 3017
3-Buten-1-ynyldiisobutylaluminium, 3549
3-Buten-1-ynyltriethyllead, 3357

* 1-Butoxyethyl 3-trimethylplumbylpropiolate, 3552

Caesium acetylide, 0614
Calcium acetylide, 0585
Copper(II) acetylide, 0615
Copper(I) benzene-1,4-bis(ethynide), 3236
Copper 1,3,5-octatrien-7-ynide, 2933
Dicopper(I) acetylide, 0619
Dicopper(I) 1,5-hexadiynide, 2165
Dimethyl(phenylethynyl)thallium, 3298
Dimethyl-1-propynylthallium, 1938
Gold(I) acetylide, 0573
Lithium acetylide, 0992
Lithium bromoacetylide, 0580
Lithium chloroacetylide, 0599
Lithium 1-heptynide, 2834

∗ Lithium 3-(1,1,2,2-tetrafluoroethoxy)propynide, 1820
Lithium trifluoropropynide, 1046
Manganese(II) bis(acetylide), 1396
Mercury(II) acetylide, 0975
Mercury bis(chloroacetylide), 1356
3-Methyl-3-buten-1-ynyltriethyllead, 3413
Monocaesium acetylide, 0661
Monolithium acetylide, 0673
∗ Monolithium acetylide–ammonia, 0674
Monopotassium acetylide, 0671
Monorubidium acetylide, 0685
Monosilver acetylide, 0650
Monosodium acetylide, 0684
1,3-Pentadiyn-1-ylcopper, 1819
1,3-Pentadiyn-1-ylsilver, 1815
Potassium acetylide, 0987
1-Propynylcopper(I), 1098
Rubidium acetylide, 1025
Silver acetylide, 0568
∗ Silver acetylide–silver nitrate, 0569
Silver buten-3-ynide, 1408
∗ Silver chloroacetylide, 0566
Silver cyclopropylacetylide, 1838
Silver 1,3,5-hexatrienide, 2052
Silver 3-hydroxypropynide, 1088
Sodium acetylide, 1022
Sodium bromoacetylide, 0581
Sodium chloroacetylide, 0601
Sodium ethoxyacetylide, 1478
Sodium methoxyacetylide, 1123
Sodium phenylacetylide, 2911
Strontium acetylide, 1026
Tetraethynylgermanium, 2895
Tetraethynyltin, 2901
Thallium(I) iodacetylide, 0984
∗ Tributyl(phenylethynyl)lead, 3811
Triethynylaluminium, 2095
Triethynylantimony, 2125
∗ Triethynylarsine, 2096

See other ACETYLENIC COMPOUNDS

DropBooks

METAL ALKOXIDES $M(OR)_n$

1. *Alkali and Alkali-Earth Metal Alkoxides*, Brochure, Troisdorf-Oberlaar, Dynamit Nobel AG, 1974

2. Hopper, S. P. *et al., Synth. React. Inorg. Metal-Org Chem.,* 1977, **7**, 162; *J. Organomet. Chem.,* 1977, **134**, 178

An appendix to the brochure is devoted to safe handling of the alkoxides indicated by a suffixed asterisk in the list below, and not all of which are represented as indexed entries with page numbers. These materials are readily hydrolysed and the exotherm may ignite the solids in presence of moist air, the potassium derivatives being the most reactive. This tendency is increased by acidic conditions, and combustion of solids spreads rapidly. Potassium *tert*-butoxide is especially reactive towards a range of liquids and solvent vapours [1]. Heating of sodium methoxide, ethoxide or potassium *tert*-butoxide (at 100°C) must always be under nitrogen to prevent ignition, which occurs in presence of air, especially if moist [2].

See Potassium *tert*-butoxide: Acids, or Reactive solvents

Dicyclopentadienylchromium: Alcohols, 3273

Individually indexed compounds are:

Aluminium isopropoxide, 3216
∗ Bis(2,4-pentanedionato)chromium, 3326
Molybdenum hexamethoxide, 2596
Potassium *tert*-butoxide, 1650
Potassium ethoxide, 0861
Potassium methoxide, 0450
∗ Potassium methylselenide, 0451
Rhenium hexamethoxide, 2603
Sodium ethoxide, 0878
Sodium isopropoxide, 1270
Sodium methoxide, 0464
∗ Sodium 2,2,2-trifluoroethoxide, 0705
∗ Tetrakis(butylthio)uranium, 3731
∗ Tetrakis(ethylthio)uranium, 3096
Titanium butoxide, 3730
Titanium(III) methoxide, 1317
Titanium tetraisopropoxide, 3579
Tungsten hexamethoxide, 2604
Zinc ethoxide, 1704

METAL AMIDOSULFATES H_2NSO_2OM

Metal nitrates or nitrites

Heubel, J. *et al., Compt. rend. [3],* 1963, **257**, 684

Heating mixtures of barium, potassium or sodium amidosulfates or amidosulfuric acid, with sodium or potassium nitrates or nitrites, leads to reactions which may be explosive. TGA plots are given.

Heating mixtures of barium, potassium or sodium amidosulfates or amidosulfuric acid, with sodium or potassium nitrates or nitrites, leads to reactions which may be explosive. TGA plots are given.

Barium amidosulfate, 0209
Potassium amidosulfate, 4457
Sodium amidosulfate, 4467
See other N–S COMPOUNDS

METAL AZIDE HALIDES **MXN_3**

Dehnicke, K., *Angew. Chem. (Intern. Ed.)*, 1967, **6**, 243
Metal halides and halogen azides react to give a range of metal azide halides, many of which are explosive. Individually indexed compounds are:
Azidopentafluorotungsten, 4358
Chromyl azide chloride, 3968
Diamminedichloroaminotrichloroplatinum(IV), 4179
Molybdenum azide tribromide, 0288
Molybdenum diazide tetrachloride, 4164
Silver azide chloride, 0009
Tin azide trichloride, 4146
Titanium azide trichloride, 4147
Titanium diazide dibromide, 0273
Tungsten azide pentabromide, 0297
Tungsten azide pentachloride, 4182
Uranium azide pentachloride, 4181
Vanadium azide tetrachloride, 4166
Vanadyl azide dichloride, 4090
See AMMINEMETAL AZIDES

DropBooks

METAL AZIDES **MN_3**

1. Mellor, 1940, Vol. 8, Suppl. 2, 16–54
2. *Energetic Materials*, Fair, H. D. and Walker, R. F. (Eds.), Vols. 1 and 2, New York, Plenum, 1977

This large and well documented group of explosive compounds contains some which are widely used industrially [1]. The text gives a thorough treatment of all aspects of the physics and chemistry (Vol. 1) and of the applications (Vol. 2) of this important group of energetic compounds [2].

Acids

The majority of the metal azides are sensitive explosives and exposure to heat, friction or impact is usually undesirable. Contact of most azides, particularly readily soluble ones, with acids will produce hydrogen azide, itself an explosive and highly toxic low-boiling liquid. In presence of heavy metals, it may give other equally hazardous heavy metal azides. These may also be formed from contact of soluble azides with heavy metals.
See Hydrogen azide

Halogenated solvents

Bretherick, L., *Chem. & Ind.*, 1986, 729; *Chem. Eng. News*, 1986, **64**(51), 2

Attention is drawn to the possibility of slow formation of explosive organic azides from long contact of halogenated solvents with metal azides.

See Dichloromethane: Azide form etc.

Relevant group entries are:

AMMINEMETAL AZIDES
AZIDE COMPLEXES OF COBALT(III)

and individually indexed compounds are:

Aluminium azide, 0082
∗ Azidogermane, 4416
Barium azide, 0214
∗ Bis(2-aminoethyl)aminecobalt(III) azide, 1775
∗ Bis(cyclopentadienyl)tungsten diazide oxide, 3285
∗ Bis(cyclopentadienyl)vanadium diazide, 3286
Cadmium azide, 3957
Caesium azide, 4262
Calcium azide, 3936
Cerium azide, 3966
∗ Chromyl azide, 4239
Cobalt(II) azide, 4216
Copper(I) azide, 4287
Copper(II) azide, 4280
∗ Copper(II) azide hydroxide, 4270
∗ Diazido-bis(1,2-diaminoethane)ruthenium(II) hexafluorophosphate, 1789
∗ Dicarbonyl-π-cycloheptatrienyltungsten azide, 3123
∗ Dicarbonylmolybdenum diazide, 0995
∗ Dicarbonyltungsten diazide, 1013
∗ Dodecamethyltetraplatinum(IV) azide, 3590
∗ Hydrogen hexaazidothallate(III), 4502
∗ Lead(IV) acetate azide, 2402
Lead (II) azide, 4782
Lead(IV) azide, 4790
Lithium azide, 4685
∗ Lithium hexaazidocuprate(4−), 4278
∗ Lithium tetraazidoaluminate, 0081
Magnesium azide, 4694
∗ Manganese(III) azide, 4702
∗ Manganese diazide hydroxide, 4433
Mercury(I) azide, 4612
Mercury(II) azide, 4604
∗ Methylcadmium azide, 0431
Nickel azide, 4777
Palladium(II) azide, 4783
∗ Pentaammineazidoruthenium(III) chloride, 4073

∗ Phenylthallium diazide, 2286
∗ Poly(dimercuryimmonium azide), 4611
Potassium azide, 4652
∗ Potassium azidopentacyanocobaltate(3−), 1809
∗ Potassium hexaazidoplatinate(IV), 4665
∗ Potassium triazidocobaltate(1−), 4212
Silver azide, 0023
Sodium azide, 4758
Sodium triazidoaurate(?), 0113
Strontium azide, 4785
∗ Tetraamminecopper(II) azide, 4277
∗ *trans*-Tetraamminediazidocobalt(III) *trans*-diamminetetraazidocobaltate(1−), 4220
∗ Tetramethylammonium azidocyanatoiodate(I), 2006
∗ Tetramethylammonium azidocyanoiodate(I), 2005
∗ Tetramethylammonium azidoselenocyanatoiodate(I), 2005
Tetramethyldigold diazide, 1739
Thallium(I) azide, 4765
∗ Thallium(I) tetraazidothallate, 4792
Zinc azide, 4786

METAL AZOTETRAZOLIDES

Reddy, G. O. *et al.*, *Thermochim. Acta*, 1983, **66**, 231−244

Of the four salts with Hg^{2+}, Pb^{2+}, Ba^{2+} and $2Na^{+}$, the thermal sensitivity and impact-, friction- and static spark-sensitivities decreased in that order, as expected. These and other entries are:

Barium 5,5′-azotetrazolide, 0577
Disodium 5,5′-azotetrazolide, 1018
∗ Disodium 5,5′-azoxytetrazolide, 1019
Lead 5,5′-azotetrazolide, 1020
Mercury 5,5′-azotetrazolide, 0980

See other TETRAZOLES

METAL CHLORATES $M(ClO_3)_n$

NSC 371, 1977

Acids

1. Mellor, 1941, Vol. 2, 315
2. Stossel, E. *et al.*, US Pat. 2 338 268, 1944

In addition to being oxidants in contact with strong acids, metal chlorates liberate explosive chlorine dioxide gas. With conc. sulfuric acid, a violent explosion may occur unless effective cooling is used [1]. Heating a moist mixture of a metal chlorate and a dibasic organic acid (tartaric or citric acid) liberates chlorine dioxide diluted with carbon dioxide [2].

DropBooks

Ammonium salts

Mixtures are incompatible.

See Ammonium chlorate

Phosphorus, or Sugar, or Sulfur

1. Black, H. K., *School Sci. Rev.*, 1963, **44**(53), 462
2. *59th Ann. Rep. HM Insp. Explos. (Cmd. 4934)*, 5, London, HMSO, 1934
3. Berger, A., *Arbeits-Schutz.*, 1934, **2**, 20
4. Taradoire, F., *Chem. Abs.*, 1938, **32**, 1455_6

The extremely hazardous nature of mixtures of metal chlorates with phosphorus, sugar or sulfur, sometimes with addition of permanganates and metal powders, frequently prepared as amateur fireworks, is stressed. Apart from being powerfully explosive, such mixtures are dangerously sensitive to friction or shock, and spontaneous ignition sometimes occurs [1]. Chlorates containing 1–2% of bromates or sulfur as impurities are liable to spontaneous explosion [3]. The danger of mixtures of chlorates with sulfur or phosphorus is such that their preparation without a Home Office licence was prohibited in the UK by Orders in Council over 50 years ago [2]. Mixtures of sulfur with lead, silver, potassium or barium chlorates ignited at 63–67, 74, 160–162 and 108–111°C, respectively [4].

Sulfur, Initiators

1. Taradoire, F., *Bull. Soc. Chim. Fr.*, 1942, **9**, 610–620
2. Ellern, 1968, 304
3. Chapman, D. *et al.*, *J. Pyrotech.*, 1997, (6), 30

The effect of initiators (diluted sulfuric acid, chlorine dioxide, sulfur dioxide or disulfur dichloride) on ignition of mixtures of barium, lead or potassium chlorates with sulfur was examined [1]. Presence of copper ion or metal (e.g. from a sieve) may also lead to explosion of such mixtures [2]. A review of hazards of sulphur/chlorate mixtures in the firework industry has been published [3].

Individually indexed compounds are:
Aluminium chlorate, 0065
Barium chlorate, 0205
Cadmium chlorate, 3952
Chloric acid, 3996
Lead(II) chlorate, 4105
Magnesium chlorate, 4083
Manganese(II) chlorate, 4087
Potassium chlorate, 4017
Silver chlorate, 0011
Sodium chlorate, 4039
Zinc chlorate, 4106

See other METAL HALOGENATES

METAL CYANATES **$M(N:C:O)_n$**

1. Singmaster, J. A., *Chem. Eng. News*, 1985, **63**(7), 2
2. Pilznienski, J. F., *Chem. Eng. News*, 1985, **63**(16), 2
3. Weast, 1979, D-67–D-79

Disregarding the differences in structure, it was argued that because the empirical formulae of fulminate and cyanate ions are identical, metal cyanates are likely to be as unstable as metal fulminates [1]. The results of practical tests, in which samples of various metal cyanates were heated in a flame, coupled with long industrial experience of the use of molten salt process baths containing over 40% of cyanates, show that the assumption on explosive instability of metal cyanates is not warranted [2]. The observation that silver or copper(II) cyanates burned smoothly on exposure to flame [2] suggests that the explosion recorded for silver cyanate (*ibid.*) may have involved close confinement or other unusual conditions during heating. Although mercury(II) cyanate (*ibid.*) vapourised gradually and completely without flaming on heating [2], two incidents of explosion during grinding or crushing operations have been recorded. The unusual tendency for many derivatives of silver and mercury to decompose forcefully (with separation of the metal, rather than the oxide as with other metals), suggests that other metal cyanates are likely to be rather more stable. This view is supported by available thermodynamic data [3], which show that while several cyanides are endothermic compounds, the few cyanates for which figures are quoted are all exothermic compounds and unlikely to be intrinsically unstable. A few reports of mishap could involve hydrolysis of the cyanate, liberating ammonia, followed by formation of ”fulminating”noble metals.

See Mercury(II) cyanate, Potassium cyanate, Silver cyanate

See also FULMINATING METALS

DropBooks

METAL CYANIDES(AND CYANO COMPLEXES) **$M(CN)_n$, $[M(CN)_n]$**

1. von Schwartz, 1918, 399, 327; Pieters, 1957, 30
2. *Res. Rept. No. 2*. New York, Nat. Board Fire Underwriters, 1950

Several members of this (often endothermic) group of compounds which contain heavy metals tend to explosive instability, and most are capable of violent oxidation under appropriate circumstances. Fusion of mixtures of metal cyanides with metal chlorates, perchlorates, nitrates or nitrites causes a violent explosion [1]. Addition of one solid component (even as a residue in small amount) to another molten component is also highly dangerous [2]. Individually indexed compounds are:

∗ Ammonium hexacyanoferrate(II), 2577
∗ Barium thiocyanate, 0576
∗ μ-1,2-Bis(cyanomercurio)ethanediylidenedimercury(II), 1798
Cadmium cyanide, 0588
∗ Chromyl isocyanate, 0613
∗ Chromyl isothiocyanate, 0612
Copper(I) cyanide, 0620
Copper(II) cyanide, 0616
Copper(II) thiocyanate, 0618
∗ Dimercury dicyanide oxide, 0983

Gold(I) cyanide, 0308
Iron(III) hexacyanoferrate(4−), 3739
Lead(II) cyanide, 0999
∗ Lead(II) thiocyanate, 1000
∗ Lithium thiocyanate, 0532
∗ Mercury(II) cyanate, 0977
Mercury(II) cyanide, 0976
∗ Mercury(II) thiocyanate, 0979
Nickel(II) cyanide, 0997
∗ Potassium azidopentacyanocobaltate(3−), 1809
Potassium cyanide, 0526
Potassium hexacyanoferrate(II), 4279
Potassium hexacyanoferrate(III), 4242
Potassium octacyanodicobaltate(8−), 2880
∗ Potassium tetracyanomercurate(II), 1797
Potassium tetracyanotitanate(IV), 1800
∗ Potassium thiocyanate, 0529
∗ Silver cyanate, 0300
Silver cyanide, 0299
Sodium cyanide, 0536
∗ Sodium pentacyanonitrosylferrate(2−), 1813
∗ Sodium tetracyanatopalladate(II), 1802
∗ Sodium thiocyanate, 0538
Zinc cyanide, 1004

See also MOLTEN SALT BATHS, METAL THIOCYANATES

METAL DERIVATIVES OF ORGANOFLUORINE COMPOUNDS

Although the C-F bond is a stronger than average single covalent bond, the extreme electronegativity of fluorine makes the formation of ionic fluorides far more favourable thermodynamically. The stability of organofluorine compounds is therefore largely kinetic. Although metallated organofluorine derivatives can often be isolated they are far from thermodynamically stable and may show it. Alkoxides derived from fluorinated alcohols and phenols have also exploded. Such compounds should be treated with caution if isolated and are best handled in solution. Salts of fluorinated acids are certainly more stable and have not yet been reported as giving trouble. The metals involved are usually lithium and aluminium, but cadmium, sodium, magnesium and zirconium also feature and the thermodynamic situation changes little, whatever the metal.

See Pentafluoroethyllithium
Sodium

See FLUORINATED ORGANOLITHIUM COMPOUNDS

Many metal derivatives of nitrogenous systems containing one or more bonds linking nitrogen to a metal (usually, but not exclusively, a heavy metal) show explosive instability. Individually indexed compounds are:

∗ Amminebarium bis(nitrophenylide), 3518
Amminepentahydroxyplatinum, 4571
Ammonium nitridoosmate, 4523
Antimony(III) nitride, 4729
Barium nitride, 0219
Barium nitridoosmate, 0213
Barium perchlorylamide, 0203
Barium *N*-perchlorylbenzylamide, 3649
Bis[1,5-bis(4-methylphenyl)-1,3-pentaazadienato-N3,N5]-(T-4) cobalt, 3868
N,N-Bis(bromomercurio)hydrazine, 0268
N,N′-Bis(chloromercurio)hydrazine, 4064
Bis(dihydroxygold)imide, 0114
Bis(dimethylamino)dimethylstannane, 2597
Bismuth amide oxide, 0229
Bismuth nitride, 0230
cis-Bis(trimethylsilylamino)tellurium tetrafluoride, 2615
Cadmium amide, 3954
Cadmium nitride, 3960
Caesium amide, 4260
Caesium nitride, 4266
Caesium pentafluorotelluramide, 4257
Calcium cyanamide, 0316
Calcium nitride, 3946
Cerium nitride, 3965
Chromium nitride, 4237
Cobalt(III) amide, 4201
Cobalt(III) nitride, 4214
Copper bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3861
Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1429
Copper(I) nitride, 4289
Diamminedihydroxyosmium, 4572
∗ Dibutylthallium isocyanate, 3193
Dilithium 1,1-bis(trimethylsilyl)hydrazide, 2595
∗ Dipyridinesodium, 3280
Disilver cyanamide, 0305
Disodium *N,N′*-dimethoxysulfonyldiamide, 0911
Germanium imide, 4414
Gold(I) nitride–ammonia, 0117
Gold(III) nitride trihydrate, 0118
∗ Hexaamminecalcium, 3933
Hexafluoroisopropylideneaminolithium, 1052
∗ Hydrogen hexaazidothallate(III), 4502

DropBooks

Lead bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3862
Lead(II) imide, 4439
Lead nitride, 4753
Lithium amide, 4462
Lithium bis(trimethylsilyl)amide, 2594
Lithium diethylamide, 1686
Lithium nitride, 4688
Lithium triethylsilylamide, 2578
Magnesium nitride, 4698
Mercury(II) amide chloride, 3999
Mercury(I) cyanamide, 0523
Mercury nitride, 4615
Mercury(II) *N*-perchlorylbenzylamide, 3651
Monopotassium perchlorylamide, 3994
Nitrogen triiodide–silver amide, 4634
Nitrosylruthenium trichloride, 4144
Pentaamminedinitrogenruthenium(II) salts, 4596
Pentakis(dimethylamino)tantalum, 3384
Pentasilver diamidophosphate, 0046
Pentasilver orthodiamidophosphate, 0044
Plutonium nitride, 4726
Poly(dimercuryimmonium hydroxide), 4422
* Poly(disilicon nitride), 4757
Potassium amide, 4456
Potassium diethylamide, 1685
* Potassium dinitrogentris(trimethylphosphine)cobaltate(1−), 3228
Potassium methylamide, 0472
Potassium nitride, 4671
Potassium nitridoosmate, 4651
Potassium perchlorylamide, 4019
Potassium sulfurdiimidate, 4664
Potassium thiazate, 4648
Potassium triamidothallate ammoniate, 4551
Potassium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide, 4672
Rhenium nitride tetrafluoride, 4344
Rubidium nitride, 4727
* Seleninyl bis(dimethylamide), 1758
Silver amide, 0015
Silver 5-aminotetrazolide, 0392
Silver hexanitrodiphenylamide, 3429
Silver imide, 0030
Silver nitride, 0038
Silver *N*-nitrosulfuric diamidate, 0016
Silver *N*-perchlorylbenzylamide, 2734
Silver tetrazolide, 0366
Silver 2,4,6-tris(dioxoselena)perhydrotriazine-1,3,5-triide, 0039

3-Sodio-5-(5′-nitro-2′-furfurylideneamino)imidazolidin-2,4-dione, 2908
Sodium amide, 4465
Sodium 5-azidotetrazolide, 0551
Sodium *N*-chlorobenzenesulfonamide, 2229
Sodium diethylamide, 1688
Sodium hydrazide, 4500
Sodium nitride, 4723
Sodium tetrasulfur pentanitridate, 4775
∗ Sodium triammine, 4581
Tetrakis(dimethylamino)titanium, 3104
∗ Tetramethylammonium amide, 1782
∗ Tetraselenium tetranitride, 4771
Tetrasilver diimidodioxosulfate, 0043
Tetrasilver diimidotriphosphate, 0042
Tetrasilver orthodiamidophosphate, 0041
∗ Tetratellurium tetranitride, 4773
Thallium(I) nitride, 4731
Thallium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3-5-triide, 4761
N,N,4-Trilithioaniline, 2180
Tris(dimethylamino)antimony, 2598
Trisilver tetranitride, 0040
Tris(thionitrosyl)thallium, 4764
Trithorium tetranitride, 4774
Uranium(III) nitride, 4732
Zinc bis(1-benzeneazothiocarbonyl-2-phenyl-2-hydrazide), 3863
Zinc dihydrazide, 4563
Zirconium nitride, 4733

See METAL AZIDE HALIDES, METAL AZIDES, METAL HYDRAZIDES, NITRIDES, PERCHLORYLAMIDE SALTS

DropBooks

METAL DUSTS

1. Jacobson, M. *et al.*, *Rept. Invest. 6516(9)*, Washington, US Bur. Mines, 1961
2. Brown, H. R., *Chem. Eng. News*, 1956, **34**, 87
3. Nedin, V. V. *et al.*, *Chem. Abs.*, 1972, **77**, 167636–167641
4. Martin, R., *Powder. Metall.*, 1976, **19**, 70–73
5. Alekseev, A. G. *et al.*, *Chem. Abs.*, 1977, **86**, 175311
6. Hulanichi, S. *et al.*, *Chem. Abs.*, 1977, **87**, 87208
7. Popov, E. I. *et al.*, *Chem. Abs.*, 1981, **94**, 194483
8. Cashdollar, K. L., *Proc. Safety Progress*, 1994, **13**(3), 139.
9. Schulz, W. D., *Korrosion* (Dresden), 1986, **17620**(1), 42–44
10. Burachonok, I. N., *Chem. Abs.*, 1987, **107**, 12139
11. Boiko, V. M. *et al.*, *Arch. Combust.*, 1988, **8**(2), 101

Of the 313 samples examined, the dust explosion hazards of finely divided aluminium, aluminium–magnesium alloys, magnesium, thorium, titanium and uranium, and the hydrides of thorium and uranium, are rated highest [1]. The

need to exercise caution when handling dusts of some recently introduced reactive metals was discussed briefly. Some form explosive mixtures, not only with air or oxygen, but also with nitrogen and carbon dioxide, reacting to give the nitride or carbonate. Intimate mixtures with generally non-oxidising oxosalts may also be explosive. Beryllium, cerium, germanium, hafnium, lithium, niobium, potassium, sodium, thorium, titanium, uranium and zirconium are discussed [2]. The pyrophoric capabilities of titanium and titanium–aluminium alloys were studied, the effect of particle size on flammability and explosion parameters of aluminium and magnesium powders dispersed in air was determined, and explosion hazards of aluminium, magnesium and aluminium-based alloy powders and use of inert gas media as preventives were assessed. In a study to determine explosivity of ferrochromium, ferromanganese, ferrosilicon, ferrotitanium, manganese and calcium–silicon powders, the latter proved to be the most active [3]. Metal dust and powder explosion risks were reviewed [4], including those during spraying operations in powder production [5]. Self-ignition characteristics and explosibility parameters were determined for dusts of aluminium, lead, magnesium, zinc and aluminium–magnesium alloys [6]. More accurate results (higher values) in determination of lower concentration limit for metal dusts are obtained in a conical explosion chamber [7]. Dust explosion studies (temperature, pressure, influence of particle size) on Mg, Al, Ti, Cr, Fe, Nb, Sn, Hf, Ta, W and the non-metals B, C, Si & S are reported. Under the conditions of test, Cu, Mo, Ni and Pb were not flammable [8]. Possible reasons for an explosion in a plant using acetylene–oxygen flame spraying of aluminium, tin–lead, or zinc were analysed [9]. The relationship between particle size of tool steel powders from machining operations and ignition temperatures in air suspensions or as a bed are expressed by two equations [10]. A study of ignition of metal powders in reflected shock waves is reported [11].
Relevant group entries are:

FERROALLOY POWDERS, FINELY DIVIDED METALS, THERMITE REACTIONS

METAL FIRES

Mellottee, H., *Rév.* Gen. Therm., (Fr), 1977, **16**, 523–538

Methods of extinguishing different types of metal fires are reviewed, with 86 references.

METAL FULMINATES **MC≡N → O**

1. Urbanski, 1967, Vol. 3, 157
2. Hackspill, L. *et al., Chem. Abs.*, 1938, **32**, 4377a

The metal fulminates are all powerfully explosive. Of several salts examined, those of cadmium, copper and silver were more powerful detonators than mercury fulminate, while thallium fulminate was much more sensitive to heating and impact. Formally related salts are also explosive [1]. Sodium, potassium, rubidium and caesium fulminates are all easily detonated by feeble friction or heat. They all form double salts with mercury(II) fulminate which also explode readily, that of the rubidium salt at 45°C [2].

Individually indexed compounds are:
Cadmium fulminate, 0589
Copper(II) fulminate, 0617
∗ Dimethylthallium fulminate, 1211
Mercury(II) fulminate, 0978
Silver fulminate, 0301
Sodium fulminate, 0537
Thallium fulminate, 0539
∗ Tripropyllead fulminate, 3363

METAL HALIDES **MX_n**

Members of this group have often featured as secondary reagents in hazardous combinations of chemicals. Individually indexed compounds are:
Aluminium bromide, 0060
Aluminium chloride, 0062
Aluminium iodide, 0079
Americium trichloride, 0090
∗ Ammonium bromide, 0251
∗ Ammonium chloride, 4001
∗ Ammonium fluoride, 4299
∗ Ammonium iodide, 4512
∗ Antimony(III) chloride oxide, 4041
Antimony pentachloride, 4184
Antimony trichloride, 4157
∗ Antimony trichloride oxide, 4150
Beryllium chloride, 0221
Beryllium fluoride, 0223
∗ Bis(1-chloroethylthallium chloride) oxide, 1591
Bismuth pentafluoride, 0227
∗ *cis*-Bis(trimethylsilylamino)tellurium tetrafluoride, 2615
Caesium fluoride, 4255
Calcium bromide, 0262
Calcium chloride, 3923
∗ Chloriminovanadium trichloride, 4165
∗ Chlorogermane, 3992
Chromium(II) chloride, 4052
Chromium(III) chloride, 4127
Chromium pentafluoride, 4226
∗ Chromyl chloride, 4054
Cobalt(II) bromide, 0263
Cobalt(II) chloride, 4048
Cobalt(III) chloride, 4122
Cobalt trifluoride, 4200
Copper(I) bromide, 0265
Copper(I) chloride, 4056

DropBooks

∗ Dibromogermane, 0267
Germanium tetrachloride, 4162
Gold(III) chloride, 0111
Indium bromide, 0289
Iridium hexafluoride, 4362
Iron(II) bromide, 0266
Iron(III) bromide, 0286
Iron(II) chloride, 4061
Iron(III) chloride, 4133
Iron(II) iodide, 4395
Lead chloride, 4112
Lead(II) fluoride, 4329
Lead tetrachloride, 4172
Magnesium chloride, 4081
Manganese(II) chloride, 4085
∗ Manganese dichloride dioxide, 4086
∗ Manganese fluoride trioxide, 4301
Manganese tetrafluoride, 4343
∗ Manganese trichloride oxide, 4141
Manganese trifluoride, 4335
Mercury(II) bromide, 0269
Mercury(I) fluoride, 4312
Mercury(II) iodide, 4602
Molybdenum hexafluoride, 4365
Molybdenum pentachloride, 4180
Neptunium hexafluoride, 4366
Osmium hexafluoride, 4370
Palladium tetrafluoride, 4347
Palladium trifluoride, 4341
∗ Pentaamminechlororuthenium chloride, 4137
∗ Phenylvanadium(V) dichloride oxide, 2246
Platinum hexafluoride, 4371
Platinum tetrafluoride, 4348
Plutonium hexafluoride, 4372
Potassium chloride, 4015
∗ Potassium heptafluorotantalate(V), 4379
∗ Potassium hexafluoromanganate(IV), 4363
Potassium iodide, 4618
∗ Rhenium chloride trioxide, 4045
Rhenium hexafluoride, 4373
∗ Rhenium nitride tetrafluoride, 4344
∗ Rhenium tetrachloride oxide, 4167
Rhodium(III) chloride, 4155
Rhodium tetrafluoride, 4349
Ruthenium(III) chloride, 4156
Silver chloride, 0008

Silver difluoride, 0014
Silver fluoride, 0013
Sodium chloride, 4036
Sodium iodide, 4623
Tantalum pentachloride, 4185
Tellurium tetrabromide, 0296
Thallium, 4922
Tin(II) chloride, 4116
Tin(IV) chloride, 4174
Tin(II) fluoride, 4331
Titanium(II) chloride, 4117
Titanium dibromide, 0284
Titanium diiodide, 4630
Titanium tetrachloride, 4176
Titanium tetraiodide, 4638
Titanium trichloride, 4158
* Triethoxydialuminium tribromide, 2555
* Triethyldialuminium trichloride, 2556
Trirhenium nonachloride, 4196
Tungsten dichloride, 4119
Tungsten diiodide, 4631
Tungsten hexachloride, 4193
* Tungsten tetrabromide oxide, 0294
Uranium hexachloride, 4192
Uranium hexafluoride, 4375
Vanadium dichloride, 4118
* Vanadium tribromide oxide, 0292
Vanadium trichloride, 4159
* Vanadium trichloride oxide, 4151
Zinc chloride, 4120
Zinc iodide, 4632
Zirconium(II) chloride, 4121
Zirconium dibromide, 0285
Zirconium tetrachloride, 4178
Zirconium tetraiodide, 4639
Zirconium trichloride, 4160

See also METAL PNICTIDES

DropBooks

METAL–HALOCARBON INCIDENTS

1. Lenze, F. *et al., Z. Ges. Schiess- u. Sprengstoffw.*, 1932, **27**, 255, 293, 337, 373; *Chem. Ztg.*, 1932, **56**, 921–923
2. Artz, G. D. *et al., Sensitivity of Metal*—Halogenated Solvent Combinations, Rept. AD665057, Richmond (Va.), USNTIS, 1968
3. Cutler, D. P., *J. Haz. Mat.*, 1987, **17**(1), 99–108
4. U.S. Dept of Energy, 1994, HDBK-1081-94, (*Spontaneous Heating and Pyrophoricity*), 51

Various combinations of alkali- and alkaline earth-metals with halocarbon solvents were found to be highly heat- or impact-sensitive explosives [1]. Many combinations of more recently introduced metals with halocarbons have since been found hazardous, and the results of impact-testing of combinations of 9 powdered metals with 7 solvents are tabulated. Barium shavings showed the highest sensitivity [2]. Hazardous reactions of light metals (aluminium, magnesium, lithium, sodium, potassium) wuth halogenated hydrocarbons and polymers are reviewed, with 81 references [3]. Although largely a rehash of an earlier paper, a report describes several incidents in which carbon tetrachloride has contributed to ignition or explosion of zirconium, barium, sodium, uranium and plutonium [4].

Some examples of relevant incidents are:
Barium, Halocarbons, 0200
Beryllium, Halocarbons, 0220
† Bromomethane, Metals, 0429
Chloroform, Metals, 0372
Plutonium, Carbon tetrachloride, 4888
Samarium, 1,1,2-Trichlorotrifluoroethane, 4911
Tin, Carbon tetrachloride, Water, 4912
Titanium, Halocarbons, 4919
Uranium, Carbon tetrachloride, 4923
Zirconium, Carbon tetrachloride, 4928

See also HALOCARBONS: METALS

METAL HALOGENATES $M(XO_3)_n$

Metals and oxidisable derivatives, or
Non-metals, or Oxidisable materials

1. Mellor, 1946, Vol. 2, 310; 1956, Vol. 2, Suppl. 1, 583–584; 1941, Vol. 3, 651
2. von Schwartz, 1918, 323

Intimate mixtures of chlorates, bromates or iodates of barium, cadmium, calcium, magnesium, potassium, sodium or zinc, with finely divided aluminium, arsenic, copper; carbon, phosphorus, sulfur; hydrides of alkali- and alkaline earth-metals; sulfides of antimony, arsenic, copper or tin; metal cyanides, thiocyanates; or impure manganese dioxide may react violently or explosively, either spontaneously (especially in presence of moisture) or on initiation by heat, friction, impact, sparks or addition of sulfuric acid [1]. Mixtures of sodium or potassium chlorate with sulfur or phosphorus are rated as being exceptionally dangerous on frictional initiation.

See METAL CHLORATES

Individually indexed compounds are:
Barium bromate, 0202
Barium iodate, Barium iodate, 0211
Bromic acid, 0248
Lead bromate, 0278

Mercury(I) bromate, 0271
Potassium iodate, 4619
Silver iodate, 0020
Sodium iodate, 4624
Zinc bromate, 0279
See other METAL OXOHALOGENATES

METAL HYDRAZIDES $M^{n+}(HN^{-}-NH_2)_n$

Hydrazine and its Derivatives, Schmidt, F. W., New York, Wiley, 1984, 371
This class of compounds has been little studied as they tend to explode during preparation and isolation. There are entries for:
Calcium hydrazide, 3932
Lithium hydrazide, 4496
Sodium hydrazide, 4500
See also *N*-METAL DERIVATIVES

METAL HYDRIDES MH_n, $[MH_n]$

1. Banus, M. D., *Chem. Eng. News*, 1954, **32**, 2424–2427
2. Mackay, 1966, 66
3. *Metal Hydrides*, Müller, W. M. *et al.*, New York, Academic Press, 1968
4. Hariguchi, S. *et al., Chem. Abs.*, 1981, **94**, 159191
5. Vogman, L. P., *Chem. Abs.*, 1984, **101**, 116147
6. Klusever, P. A. A. *et al., Angew. Chem. (Intern. Ed.)*, 1986, **25**, 465

DropBooks

Precautions necessary for safe handling of three main groups of hydrides of commercial significance were discussed. The first group (sodium hydride, lithium or sodium tetrahydroaluminates) ignite or explode in contact with liquid water or high humidity, while the second group (lithium, calcium, strontium or barium hydrides; sodium or potassium tetrahydroborates) do not. Burning sodium hydride is reactive enough to explode with the combined water in concrete. The 3rd group ('alloy' or non-stoicheiometric hydrides of titanium, zirconium, thorium, uranium, vanadium, tantalum, and palladium) are produced commercially in very finely divided form. Though less pyrophoric than the corresponding powdered metals, once burning is established they are difficult to extinguish, and water-, carbon dioxide- or halocarbon-based extinguishers caused violent explosions. Powdered dolomite is usually effective in smothering such fires [1]. The trihydrides of the lanthanoid (rare earth) metals are pyrophoric in air and the dihydrides, though less reactive, must be handled under inert atmosphere [2]. A later reference states that finely divided metal hydrides of the second group (lithium, calcium, barium and strontium hydrides) will ignite in air or react violently, sometimes explosively, with water or air of high humidity [3]. In an examination of the lower concentration limits, explosion pressures and pressure-increase rates of a series of mixed metal hydride powders dispersed in air, hydrides of MgNi were the most hazardous [4]. The minimum oxygen concentrations for explosion of most volatile hydrides of group IIIA–VA elements is nearly zero, so complete

exclusion of air is essential for safe working. Presence of impurities in hydride mixtures increases the risk of ignition [5]. A new method of producing alkali-metal hydrides involves hydrogenation of butyllithium, butylsodium or butylpotassium in hexane–tetramethylethylenediamine. The hydrides so produced are superactive with a wide range of materials, and of course immediately pyrophoric in air [6].

Individually indexed compounds of this group of active reducants are:

∗ Aluminium hydride–diethyl ether, 0073
∗ Aluminium hydride–trimethylamine, 0072
∗ Azidogermane, 4416
Barium hydride, 0207
Beryllium hydride, 0224
∗ Bromogermane, 0246
Cadmium hydride, 3953
Caesium hydride, 4258
Calcium hydride, 3927
Cerium dihydride, 3962
Cerium trihydride, 3963
∗ Chlorogermane, 3992
Copper(I) hydride, 4286
∗ Dibromogermane, 0267
Digallane, 4410
† Digermane, 4420
† Germane, 4417
† Hydrogen telluride, 4488
Lanthanum dihydride, 4461
Lanthanum hydride, 4495
∗ Lithium diphenylhydridotungstate(2−), 3503
Lithium hydride, 4432
Magnesium hydride, 4463
Magnesium–nickel hydride, 4464
Plutonium(III) hydride, 4509
Poly(germanium dihydride), 4415
Poly(germanium monohydride), 4413
Potassium hydride, 4427
Rubidium hydride, 4450
Sodium hydride, 4444
† Stibine, 4510
Thorium dihydride, 4489
Thorium hydride, 4540
Titanium dihydride, 4490
Titanium–zirconium hydride, 4491
Trigermane, 4421
Uranium(III) hydride, 4511
Uranium(IV) hydride, 4541

Zinc hydride, 4492
'Zirconium hydride', 4493
See COMPLEX HYDRIDES, PYROPHORIC MATERIALS
See entry LANTHANIDE–TRANSITION METAL ALLOY HYDRIDES

METAL HYPOCHLORITES $M(OCl)_n$

A widely used group of industrial oxidants which has been involved in numerous incidents, some with nitrogenous materials leading to formation of nitrogen trichloride.
See BLEACHING POWDER

and the individually indexed compounds:
Calcium hypochlorite, 3924
Lead(II) hypochlorite, 4098
Magnesium hypochlorite, 4082
Sodium hypochlorite, 4037
See Chlorine: Nitrogen compounds

Amines
Kirk-Othmer, 1963, Vol. 2, 104
Primary or secondary amines react with sodium or calcium hypochlorites to give *N*-chloroamines, some of which are explosive when isolated. Application of other chlorinating agents to amines or their precursors may also produce the same result under appropriate conditions.
See related HYPOHALITES *See other* METAL OXOHALOGENATES

DropBooks

METALLURGICAL SAMPLE PREPARATION

Standard methods of preparing samples for metallurgical examination sometimes involve extremely hazardous combinations of oxidants, such as nitric or perchloric acid, and organic solvents. These are frequently destabilised by metal catalysis. Resultant incidents will be recorded under the entry for the oxidant in question.

METAL NITRATES $M(NO_3)_n$

Aluminium
See Aluminium: Metal nitrates, etc.

Citric acid
Shannon, I. R., *Chem. & Ind.*, 1970, 149
During vacuum evaporation of an aqueous mixture of unspecified mixed metal nitrates and citric acid, the amorphous solid exploded when nearly dry. This was attributed to oxidation of the organic residue by the nitrates present, possibly catalysed by one of the oxides expected to be produced.

Esters, or Phosphorus, or Tin(II) chloride
Pieters, 1957, 30

Mixtures of metal nitrates with alkyl esters may explode, owing to formation of alkyl nitrates. Mixtures of a nitrate with phosphorus, tin(II) chloride or other reducing agents (i.e. redox combinations) may react explosively.
See other REDOX REACTIONS

Ethanol

Pitwell, L. R., *Chem. Eng. News*, 1978, **56**(37), 56
In the analysis of water, the use of ethanol to remove more than traces of nitrate or nitrite ion may lead to formation of fulminic acid, and if mercury(II) is used as a catalyst, explosive mercury fulminate may be formed.
See Mercury(II) nitrate: Ethanol
Silver nitrate: Ethanol, 0022

Metal phosphinates

1. Mellor, 1940, Vol. 8, 881
2. Costa, R. L., *Chem. Eng. News*, 1947, **25**, 3177

Mixtures of metal nitrates and phosphinates, previously proposed as explosives [1], explode on heating.

Organic matter

1. Bowen, H. J. M., *Anal. Chem.*, 1968, **40**, 969; private comm., 1968
2. Grewelling, T., *Anal., Chem.*, 1969, **41**, 540–541
3. Crutchfield, C. A. *et al., J. Chem. Ed.*, 1991, **68**(7), 620
4. Editor's comments

When organic matter is destroyed for residue analysis by heating with equimolar potassium nitrate–sodium nitrate mixture to 390°C, a 20-fold excess of nitrate must be used. If over 10% of organic matter is present, pyrotechnic reactions occur which could be explosive [1]. Subsequent to an explosion while a citric acid–sodium nitrate mixture was being heated at below 500°C, experiments on the effect of heating various organic materials with metal nitrates showed the tendency for explosion to increase from magnesium through calcium to sodium nitrate. This is in the order of m.p. of the nitrates, and explosion may occur when the nitrates melt and make intimate contact with the organic matter. Pretreatment with nitric acid may reduce the explosion risk [2]. A slurry of nickel nitrate, starch, an amine and some presumably inert components proved to be a deflagrating explosive when cyclone dried, igniting above 135°C. Caution is advised when mixing nitrates with oxidisable materials [3].

Recent accidents suggest that the scientific world needs to be reminded that for the first 500 years of firearms and the first 300 of civil blasting the only explosive available was a mixture of one of the more stable and less oxidising metal nitrates with not very combustible carbonaceous material plus a catalyst. Gunpowder has been largely replaced by safer and more reliable explosives, but similar mixes remain unsafe because potentially explosive, especially if the mixing is at the molecular level in a complex. Substitutes for gunpowder are occasionally patented, they often consist of a carbohydrate and a metal nitrate. It cannot always be assumed that the safety of metal nitrates is the greater when they are hydrated [4].

See Citric acid, above
See also Copper(II) nitrate

Potassium hexanitrocobaltate
See Potassium hexanitrocobaltate(3−)

Vinyl sulfones
See VINYL SULFOXIDES

Individually indexed compounds are:
∗ Ammonium hexanitrocerate, 3964
∗ Ammonium nitrate, 4522
Barium nitrate, 0212
Caesium nitrate, 4261
Calcium nitrate, 3935
∗ Chromyl nitrate, 4238
Cobalt(II) nitrate, 4215
∗ Copper(II) glycinate nitrate, 0905
Copper(II) nitrate, 4279
∗ Dimethyltin dinitrate, 0914
∗ Heptasilver nitrate octaoxide, 0047
∗ 2-Hydroxyethylmercury(II) nitrate, 0857
Iron(III) nitrate, 4397
Lead(II) nitrate, 4749
Lithium nitrate, 4684
Magnesium nitrate, 4693
Manganese(II) nitrate, 4701
Mercury(I) nitrate, 4609
Mercury(II) nitrate, 4603
∗ 2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane, 1592
Nickel(II) nitrate, 4743
Plutonium(IV) nitrate, 4768
Potassium nitrate, 4650
Silver nitrate, 0022
Sodium hexaoxodinitrate, 4740
Sodium nitrate, 4721
Sodium pentaoxodinitrate, 4739
Sodium tetraoxodinitrate, 4738
Sodium trioxodinitrate, 4737
∗ Tetrahydroxotritin(2+) nitrate, 4525
Thallium(III) nitrate, 4762
Tin(II) nitrate, 4750
∗ Triethylphosphinegold nitrate, 2558
Uranyl nitrate, 4752
∗ Vanadium trinitrate oxide, 4763
Zinc nitrate, 4751
See MOLTEN SALT BATHS *See other* METAL OXO-NONMETALLATES

DropBooks

METAL NITRITES $M(NO_2)_n$

Metal Cyanides
See Sodium nitrite: Metal cyanides

Nitrogenous bases
Metal nitrites react with salts of nitrogenous bases to give the corresponding nitrite salts, many of which are unstable.
See NITRITE SALTS OF NITROGENOUS BASES

Potassium hexanitrocobaltate
See Potassium hexanitrocobaltate(3−)

Individually indexed compounds are:
Magnesium nitrite, 4692
∗ Nitritonitrosylnickel, 4742
∗ Potassium hexanitrocobaltate(3−), 4213
Potassium nitrite, 4649
Sodium nitrite, 4720
See MOLTEN SALT BATHS *See other* METAL OXONON-METALLATES, OXIDANTS

METAL NITROPHENOXIDES $O_2NC_6H_4OM$

Author's comments, 1988
Several metal salts of nitrophenols exhibit very limited thermal stability, especially heavy metal salts, and several instances of explosive decomposition at modest (or even ambient) temperatures have been recorded. Individual entries are:
∗ Cobalt(II) picramate, 3460
∗ Lead 2-amino-4,6-dinitrophenoxide, 3469
Lead 2,4,6-trinitroresorcinoxide, 2071
∗ Lithium 4-nitrothiophenoxide, 2177
Manganese picrate hydroxide, 3742
Nickel 2,4-dinitrophenoxide hydroxide, 3745
Nickel 2-nitrophenoxide, 3464
4-Nitrophenol, : Potassium hydroxide, 2267
Potassium 4-nitrophenoxide, 2174
Silver 2-azido-4,6-dinitrophenoxide, 2075
∗ Silver 4-nitrophenoxide, 2126
Sodium 2,4-dinitrophenoxide, 2115
Sodium 4-nitrophenoxide, 2183
∗ Sodium 2-nitrothiophenoxide, 2182
Sodium picrate, 2086
Thallium(I) 2- or 4-nitrophenoxide, 0543
See PICRATES

This class includes the products of combination of metals and non-metals except C (as acetylene), H, N, O, and S, which are separately treated in the groups:

METAL ACETYLIDES
N-METAL DERIVATIVES
METAL HYDRIDES
METAL OXIDES
METAL SULFIDES
NITRIDES

Individually indexed compounds are:

Aluminium carbide, 1031
Aluminium phosphide, 0083
Bismuth nitride, 0230
Caesium graphite, 2882
Calcium disilicide, 3944
Calcium phosphide, 3947
Calcium silicide, 3943
Copper diphosphide, 4284
Copper monophosphide, 4283
Copper(II) phosphide, 4290
Dialuminium octavanadium tridecasilicide, 0088
Dicobalt boride, 0128
Ditungsten carbide, 0564
∗ Ferrosilicon, 4390
Hexalithium disilicide, 4689
Iron carbide, 0365
Lanthanum carbide, 0991
Lead pentaphosphide, 4881
Lithium heptapotassium di(tetrasilicide), 4676
Lithium tripotassium tetrasilicide, 4675
Magnesium boride, 0168
Magnesium nitride, 4698
Magnesium phosphide, 4699
Magnesium silicide, 4697
Manganese phosphide, 4711
Manganese(II) telluride, 4708
Platinum diarsenide, 0107
Potassium graphite, 3107
Potassium silicide, 4658
Rubidium graphite, 3110
Sodium phosphide, 4815
Sodium silicide, 4801
∗ Tetraamminelithium dihydrogenphosphide, 4595
Thorium dicarbide, 1027
Titanium carbide, 0561

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Trimercury tetraphosphide, 4616
Tungsten carbide, 0563
Uranium carbide, 0562
Uranium dicarbide, 1028
Zinc phosphide, 4876
Zirconium dicarbide, 1029
METAL PNICTIDES

METAL OXALATES **$(MOCO.-)_2$**

Mellor, 1941, Vol. 1, 706

The tendency for explosive decomposition of heavy metal oxalates is related to the value of the heat of decomposition. Individually entries are:

Copper(I) oxalate, 0622
Iron(III) oxalate, 2065
Mercury(II) oxalate, 0982
∗ Potassium dinitrooxalatoplatinate(2−), 0988
Silver oxalate, 0572

See other HEAVY METAL DERIVATIVES

METAL OXIDES **MO_n**

Malinin, G. V. *et al.*, *Russ. Chem. Rev.*, 1975, **44**, 392−397

Thermal decomposition of metal oxides was reviewed. Some oxides (cobalt(II, III) oxide, copper(II) oxide, lead(II, IV) oxide, uranium dioxide, triuranium octaoxide) liberate quite a high proportion of atomic oxygen, with a correspondingly higher potential for oxidation of fuels than molecular oxygen.

This large group covers a wide range of types of reactivity and there is a separate entry for the related group:

See also METAL PEROXIDES

Individually indexed compounds are:

Aluminium oxide, 0087
∗ Antimony(III) chloride oxide, 4041
Antimony(III) oxide, 4851
∗ Antimony trichloride oxide, 4150
Barium oxide, 0215
Beryllium oxide, 0225
∗ Bis(1-chloroethylthallium chloride) oxide, 1591
Bismuth trioxide, 0233
∗ Bis(trimethylsilyl) chromate, 2591
Cadmium oxide, 3958
Caesium oxide, 4264
Caesium trioxide, 4263
Calcium oxide, 3937
Chromium(II) oxide, 4241
Chromium(III) oxide, 4251

Chromium trioxide, 4242
Cobalt(II) oxide, 4217
Cobalt(III) oxide, 4221
Copper(I) oxide, 4288
Copper(II) oxide, 4281
Dibismuth dichromium nonaoxide, 0232
Dilead(II)lead(IV) oxide, 4861
Disilver pentatin undecaoxide, 0036
Gallium(I) oxide, 4411
Indium(II) oxide, 4641
Iridium(IV) oxide, 4644
Iron(II) oxide, 4398
Iron(III) oxide, 4403
Iron(II,III) oxide, 4405
Lanthanum oxide, 4679
Lead(II) oxide, 4824
Lead(IV) oxide, 4834
Magnesium oxide, 4695
∗ Manganese chloride trioxide, 4022
∗ Manganese dichloride dioxide, 4086
∗ Manganese fluoride trioxide, 4301
Manganese(II) oxide, 4704
Manganese(IV) oxide, 4705
Manganese(VII) oxide, 4709
∗ Manganese trichloride oxide, 4141
‘Mercury(I) oxide’, 4613
Mercury(II) oxide, 4605
Molybdenum(IV) oxide, 4716
Molybdenum(VI) oxide, 4717
Nickel(II) oxide, 4821
Nickel(III) oxide, 4823
Nickel(IV) oxide, 4822
Niobium(V) oxide, 4818
Osmium(IV) oxide, 4833
Osmium(VIII) oxide, 4858
Palladium(II) oxide, 4825
Palladium(III) oxide, 4848
Palladium(IV) oxide, 4835
∗ Phenyliodine(III) chromate, 2247
Platinum(IV) oxide, 4836
∗ Potassium dioxide, 4656
∗ Potassium trioxide, 4657
∗ Rhenium chloride trioxide, 4045
∗ Rhenium tetrachloride oxide, 4167
Ruthenium(VIII) oxide, 4862
∗ Selenium dioxide, 4838

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Silver(I) oxide, 0032
Silver(II) oxide, 0025
∗ Sodium dioxide, 4799
Sodium oxide, 4802
∗ Sodium trioxide, 4800
Tantalum(V) oxide, 4865
Thallium(III) oxide, 4854
∗ Thorium oxide sulfide, 4826
Tin(II) oxide, 4829
Tin(IV) oxide, 4840
Titanium(IV) oxide, 4842
Triuranium octaoxide, 4871
Tungsten(IV) oxide, 4844
Tungsten(VI) oxide, 4856
∗ Undecaamminetetraruthenium dodecaoxide, 4598
Uranium(IV) oxide, 4843
Vanadium(III) oxide, 4855
Vanadium(V) oxide, 4866
∗ Vanadium trichloride oxide, 4151
Zinc oxide, 4830
∗ Zirconium oxide sulfide, 4827

METAL OXOHALOGENATES MXO_n

Solymosi, F., *Acta Phys. Chem.*, 1976, **22**, 75–115

This class covers the four levels of oxidation represented in the series hypochlorite, chlorite, chlorate and perchlorate, and as expected, the oxidising power of the anion is roughly proportional to the oxygen content, though stability factors are also important. The class has been subdivided under the group headings below, each of which has its own listing of member compounds.

METAL HYPOCHLORITES, CHLORITE SALTS
METAL HALOGENATES, METAL PERCHLORATES

Some individually indexed compounds are:

∗ Ammonium iodate, 4513
∗ Ammonium periodate, 4514
Cadmium chlorate, 3952
Calcium chlorite, 3925
∗ Lead acetate–lead bromate, 1540
Lead(II) chlorite, 4102
Mercury(II) bromate, 0270
Potassium bromate, 0255
Potassium chlorate, 4017
Potassium periodate, 4620
Silver bromate, 0007
Sodium bromate, 0257

Sodium chlorite, 4038
Thallium bromate, 0260

METAL OXOMETALLATES $M^+ MO_n^-$

Salts with oxometallate anions function as oxidants, those with oxygen present as peroxo groups being naturally the more powerful, and separately grouped under
See also PEROXOACID SALTS

Individually indexed oxometallate salts are:

∗ Bis(benzene)chromium dichromate, 3851
Calcium chromate, 3926
Copper chromate oxide, 4223
Dibismuth dichromium nonaoxide, 0232
Lead chromate, 4243
Lithium chromate, 4236
Magnesium permanganate, 4691
Potassium dichromate, 4248
Potassium permanganate, 4647
Sodium dichromate, 4250
Sodium molybdate, 4713
Sodium permanganate, 4703
Zinc permanganate, 4710

METAL OXONON-METALLATES $M^+ EO_n^-$

DropBooks

This large and commonly used class of salts covers a wide range of oxidising potential. Among the more powerful oxidants are those grouped under

METAL OXOHALOGENATES
PEROXOACID SALTS
METAL NITRITES
METAL NITRATES
METAL SULFATES
METAL AMIDOSULFATES

for which separate entries emphasise the individual features. Some less highly oxidised anions function as reducants which also have a separate entry. Individually indexed entries are:

∗ Ammonium iron(III) sulfate, 4393
∗ Ammonium sulfate, 4574
Barium sulfate, 0217
Calcium sulfate, 3939
Chromium(II) sulfate, 4244
Copper(II) phosphinate, 4272
Copper(II) sulfate, 4282
Iron(II) sulfate, 4399
Lead sulfate, 4860

Lithium carbonate, 0533
Lithium dithionite, 4687
Magnesium carbonate hydroxide, 0534
Magnesium nitrate, 4693
Magnesium nitrite, 4692
Magnesium sulfate, 4696
Potassium carbonate, 0531
Potassium nitrite, 4649
Silver hyponitrite, 0031
Sodium acetate, 0779
Sodium carbonate, 0552
Sodium disulfite, 4808
Sodium dithionite, 4807
Sodium hydrogen carbonate, 0390
Sodium hydrogen sulfate, 4446
Sodium metasilicate, 4805
Sodium nitrite, 4720
Sodium sulfate, 4806
∗ Sodium tetraborate, 0185
Sodium thiosulfate, 4804

METAL PERCHLORATES **$M(ClO_4)_n$**

1. Burton, M., *Chem. Eng. News*, 1970, **48**(51), 55
2. Cook, R. E. *et al., J. Chem. Res.*, 1982, (S) 267; (M) 2772–2783

Though metal perbromates and periodates are known (but not perfluorates), the perchlorates have most frequently been involved in hazardous incidents over a long period. These usually stable salts are powerful oxidants and contact with combustible materials or reducants must be under controlled conditions. A severe restriction on the use of metal perchlorates in laboratory work has been recommended [1]. Attention has been drawn, on the basis of experience with cobalt(II) perchlorate, to the possibility of stable hydrated metal perchlorates being converted by unintentional dehydration to unstable (endothermic) lower hydrates capable of explosive decomposition in absence of impurities. Great care to avoid dehydration (or desolvation) is urged [2].

See SOLVATED OXOSALT INCIDENTS

Calcium hydride

Mellor, 1941, Vol. 3, 651

Rubbing a mixture of calcium (or strontium) hydride with a metal perchlorate in a mortar causes a violent explosion.

See other REDOX REACTIONS

Organic ligands

Nair, M. R. G. *et al., Talanta*, 1981, **28**, 395–396

A safe method for decomposing complexes of various organic ligands with metal perchlorates prior to analysis involves heating them with ammonium chloride, but

this method should be tested on the small scale when applied to complexes not previously decomposed in this way.
See AMMINEMETAL OXOSALTS

Sulfuric acid
Pieters, 1957, 30; Schumacher, 1960, 190
Metal perchlorates with highly concentrated or anhydrous acid form the explosively unstable anhydrous perchloric acid.
See Perchloric acid: Dehydrating agents

Trifluoromethanesulfonic acid
See Trifluoromethanesulfonic acid: Perchlorate salts

Individually indexed metal perchlorates are:
† Acetonitrile, : Lanthanide perchlorate, 0758
∗ Acetoxydimercurio(perchloratodimercurio)ethenone, 1413
∗ Acetoxymercurio(perchloratomercurio)ethenone, 1412
Aluminium perchlorate, 0066
∗ Antimony(III) oxide perchlorate, 4046
Barium perchlorate, 0206
∗ (Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2614
Beryllium perchlorate, 0222
∗ 1,1-Bis(dimethyl sulfoxide)telluracyclopentane diperchlorate, 1588
Chromium(III) perchlorate . 6 dimethyl sulfoxide, 4130
∗ Chromyl perchlorate, 4055
Cobalt(II) perchlorate hydrates, 4051
Copper(I) perchlorate, 4058
Copper(II) perchlorate, 4057
∗ Cyclopentadiene–silver perchlorate, 1859
∗ Diethylthallium perchlorate, 1682
∗ Dodecamethyltetraplatinum(IV) perchlorate, 3587
Dysprosium perchlorate, 4131
Erbium perchlorate, 4132
∗ Ethylphenylthallium(III) acetate perchlorate, 3302
Gallium perchlorate, 4135
Indium(I) perchlorate, 4014
Iron(II) perchlorate, 4062
Iron(III) perchlorate, 4134
Lead perchlorate, 4108
Lithium perchlorate, 4021
Magnesium perchlorate, 4084
Manganese(II) perchlorate, 4088
Mercury(II) perchlorate, 4078
Mercury(II) perchlorate . 6 (or 4)dimethyl sulfoxide, 4079
∗ Methylmercury perchlorate, 0433
Neodymium perchlorate . 2 acetonitrile, 4148

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Nickel perchlorate, 4094
∗ Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3778
Potassium perchlorate, 4018
Silver perchlorate, 0012
Sodium perchlorate, 4040
∗ Tetrasulfurtetraimide–silver perchlorate, 0029
Tetrazirconium tetraoxide hydrogen nonaperchlorate, 4195
Tin(II) perchlorate, 4109
Titanium tetraperchlorate, 4170
Uranyl perchlorate, 4111
Vanadyl perchlorate, 4152

See other METAL OXOHALOGENATES

METAL PEROXIDES $M(O_2)_n$

1. Castrantas, 1965, 1,4
2. Bailar, 1973, Vol. 2, 784

This group contains many powerful oxidants, the most common being sodium peroxide. Undoubtedly one of the most hazardous is potassium dioxide or superoxide, readily formed on exposure of the metal to air (but as the monovalent O_2^- ion it is not a true peroxide). Many transition metal peroxides are dangerously explosive. Individually indexed peroxides are:

Barium peroxide, 0216
Calcium peroxide, 3938
Mercury peroxide, 4606
∗ Oxodiperoxomolybdenum–hexamethylphosphoramide, 4718
∗ Potassium dioxide, 4656
Potassium peroxide, 4666
∗ Potassium trioxide, 4657
Silver peroxide, 0033
∗ Sodium dioxide, 4799
Sodium peroxide, 4803
∗ Sodium trioxide, 4800
Strontium peroxide, 4841
Zinc peroxide, 4845

See also AMMINECHROMIUM PEROXOCOMPLEXES

METAL PEROXOMOLYBDATES $M_2^+ [Mo(O_2)_4]^{2-}$

See other PEROXOMOLYBDATES AND TUNGSTATES

METAL PHOSPHINATES $M[OP(:O)H_2]_n$

This is a group of powerful reducants, several of which are of rather limited stability. Individually indexed compounds are:

Aluminium phosphinate, 0078
Barium phosphinate, 0210

Calcium phosphinate, 3931
Copper(II) phosphinate, 4272
Dipotassium phosphinate, 4431
Iron(III) phosphinate, 4394
Lead(II) phosphinate, 4531
Magnesium phosphinate, 4517
Manganese(II) phosphinate, 4519
Potassium phosphinate, 4431
Silver phosphinate, 0017
Sodium phosphinate, 4473
See other REDUCANTS

METAL PHOSPHORUS TRISULFIDES **M_3PS_3**

Clement, R. *et al., J. Chem. Soc., Dalton Trans.*, 1979, 1566
When very finely divided metals (iron, manganese, nickel or zinc) are heated with elemental phosphorus and sulfur in evacuated ampoules to form the title compounds, explosions may occur, even at temperatures as low as 150–200°C.

METAL PICRAMATES **$H_2N(O_2N)_2C_6H_2OM$**

Srivastava, R. S. *et al., Chem. Abs.*, 1979, **91**, 76315
Explosive properties of palladium(II) and uranyl picramates were determined.
See other HEAVY METAL DERIVATIVES, POLYNITROARYL COMPOUNDS

DropBooks

METAL PNICTIDES

Preparative hazard
1. Hector, A. L. *et al., Z. Naturforsch. B: Chem. Sci.*, 1994, **49**(4), 477
2. Hector, A. *et al., J. Mater. Sci. Lett.*, 1994, **13**(1), 1
3. Hector, A. *et al., Polyhedron*, 1995, **14**(7), 913

(No, the editor didn't know what this name meant either.) It means salts of the trivalent anions of Group V, restricted in [1] to arsenides, antimonides and bismuthides and prepared by reaction of sodium pnictides with anhydrous halides of transition and lanthanide metals. This violently exothermic reaction may initiate as low as 25°C. Avoidance of hydrated halides is cautioned since these are likely to react uncontrollably on mixing. Another paper includes a similar reaction of phosphides, initiated by grinding [2]. Nitrides are reported made from the thermally initiated reaction of sodium azide with metal halides, a very large sealed ampoule is counselled to contain the nitrogen [3].
See Sodium azide
See METAL NON-METALLIDES
METAL HALIDES
METATHESIS REACTIONS

METAL POLYHALOHALOGENATES **$M^+ [XX'_n]$**

Organic solvents, or Water

1. Whitney, E. D. *et al., J. Amer. Chem. Soc*., 1964, **86**, 2583
2. Sharpe, A. G. *et al., J. Chem. Soc.*, 1948, 2135

Potassium, rubidium and caesium tetrafluorochlorates and hexafluorobromates react violently with water, and explosively with common organic solvents, like the parent halogen fluorides [1]. Silver and barium tetrafluorobromates ignite in contact with ether, acetone, dioxane and petrol [2]. Individual entries are:

Barium tetrafluorobromate, 0201
Caesium hexafluorobromate, 0236
Caesium tetrafluorochlorate(1−), 3969
Potassium hexafluorobromate, 0244
Potassium tetrafluorochlorate(1−), 3984
Rubidium hexafluorobromate, 0245
Rubidium tetrafluorochlorate(1−), 3988
Silver tetrafluorobromate, 0006

METAL PYRUVATE NITROPHENYLHYDRAZONES
$MOCO.CC(Me)=NNHC_6H_4NO_2$

Ragno, M., *Gazz. Chim. Ital.*, 1945, **75**, 186−192

A wide range of the title salts of mono-, di- and tri-valent metals, with an *o*-, *m*- or *p*-nitro group present showed unstable or explosive behaviour on heating. The lead salt exploded violently at 240°C, while the aluminium, beryllium and silver salts are only feebly explosive.

See other NITROARYL COMPOUNDS

METALS **M**

Individually indexed metals are:

Aluminium, 0048
Antimony, 4907
Barium, 0200
Beryllium, 0220
Bismuth, 0226
Cadmium, 3949
Caesium, 4254
Calcium, 3922
Cerium, 3961
Chromium, 4222
Cobalt, 4199
Copper, 4267
Europium, 4292
Gallium, 4406
Germanium, 4412

Gold, 0110
Hafnium, 4599
Indium, 4640
Iridium, 4643
Lanthanum, 4677
Lead, 4882
Lithium, 4680
Magnesium, 4690
Manganese, 4700
Mercury, 4600
Molybdenum, 4712
Neodymium, 4819
Nickel, 4820
Niobium, 4817
Osmium, 4873
Palladium, 4885
Platinum, 4887
Plutonium, 4888
Potassium, 4645
Praseodymium, 4886
Rhenium, 4890
Rhodium, 4892
Rubidium, 4889
Ruthenium, 4894
Samarium, 4911
∗ Selenium, 4908
∗ Silicon, 4909
Silver, 0001
Sodium, 4796
Strontium, 4913
Tantalum, 4914
Technetium, 4915
∗ Tellurium, 4916
Thallium, 4922
Thorium, 4917
Tin, 4912
Titanium, 4919
Tungsten, 4925
Uranium, 4923
Vanadium, 4924
Zinc, 4927
Zirconium, 4928

Halocarbons
See entry METAL–HALOCARBON INCIDENTS

DropBooks

Other groups or topics related to this group are:

ALKALI-METAL ALLOYS, ALKALI METALS
DEVARDA'S ALLOY, FERROALLOY POWDERS
FINELY DIVIDED METALS, LANTHANIDE METALS
LIGHT ALLOYS, METAL DUSTS
METAL FIRES, MILD STEEL
MOLTEN METAL EXPLOSIONS, PRECIOUS METAL DERIVATIVES
PYROPHORIC METALS, REACTIVE METALS
STEEL WOOL, THORIUM FURNACE RESIDUES

METAL SALICYLATES

Nitric acid

See Nitric acid: Metal salicylates

METAL SALTS

By far the largest class of compound in this Handbook, the metal (and ammonium) salts have been allocated into two sub-classes dependent on the presence or absence of oxygen in the anion.

The main groupings adopted for the non-oxygenated salts are:

METAL ACETYLIDES, METAL AZIDE HALIDES
METAL AZIDES, METAL AZOTETRAZOLIDES
METAL CYANIDES (AND CYANO COMPLEXES)
N-METAL DERIVATIVES, METAL HALIDES
METAL POLYHALOHALOGENATES, METAL THIOCYANATES

and for the oxosalts:

METAL ABIETATES, METAL FULMINATES,
METAL NITROPHENOXIDES, METAL OXALATES
METAL PYRUVATE NITROPHENYLHYDRAZONES
METAL OXOHALOGENATES (anion an oxo derivative of a halogen)
METAL OXOMETALLATES (anion an oxo derivative of a metal)
METAL OXONON-METALLATES (anion an oxo derivative of a non-metal)
PEROXOACID SALTS (anion a peroxo derivative of a metal or non-metal)

There is a separate entry for

OXOSALTS OF NITROGENOUS BASES

In some cases it has been convenient to sub-divide the oxosalt groups into smaller sub-groups, and such sub-division is indicated under the appropriate group heading.

METAL SULFATES $M(SO_4)_n$

Aluminium

See Aluminium: Metal oxides, etc.

Magnesium

See Magnesium: Metal oxosalts

See other METAL OXONON-METALLATES

METAL SULFIDES M_mS_n

1. Byberg, K. G., *CANAMET Spec. Publ. SP87-3*, 1987, I 1.1–1.39
2. Nel, L. D., *ibid*, I 2.1–2.24
3. Hermann, F. W., *ibid*, I 3.1–3.7
4. Wheeland, K. G., *ibid*, I(B4) 5.1–5.48
5. Enright, R. J., *ibid*, II(viia) 27–44
6. Hall, A. E. (Ed.), *Sulphide Dust Explos.* Proc. Spec. Sess. CIM Ann. Gen. Meeting, Montreal, Canadian Inst. Min. Metall., 1989
7. Liu, Q. et al., *ibid.*, 125–49
8. Rosenblum, F. et al., *CIM Bull.*, 1995, **88**(989), 44; *Chem. Abs.*, 1995, **123**, 178477g

In a special publication devoted to sulfide ore dust explosions, a dust explosion in a copper–zinc sulfide mine is discussed and related to causes and preventive measures [1]. Control measures [2] and prevention of secondary explosions are also discussed [3], and surveyed, including the need for further work [4]. The results of experimental work on the use of limestone dust to suppress explosions in pyrites dusts are presented [5]. For another special publication on ore dust explosion with numerous incidents and further studies on mechanism and control see [6]. Explosibility declines in the order pyrrotite, pyrite, chalcopyrite, sphalerite, covellite, chalcocite, galena. Pyrite at 1000 g/m^3 can give a peak pressure of 5.8 bar [7]. Self heating of broken sulfide ore, to possible ignition, has been studied. Pyrrhotite seems primarily responsible [8].

See DUST EXPLOSION INCIDENTS

DropBooks

Some metal sulfides are so readily oxidised as to be pyrophoric in air. Individually indexed compounds are:

Aluminium copper(I) sulfide, 0084
∗ Ammonium sulfide, 4577
Antimony trisulfide, 4906
Barium sulfide, 0218
Bismuth trisulfide, 0234
∗ Cadmium selenide, 3959
∗ Caesium selenide, 4265
Calcium polysulfide, 3942
Calcium sulfide, 3941
Cerium trisulfide, 3967
Chromium(II) sulfide, 4245
Cobalt(II) sulfide, 4218
Copper iron(II) sulfide, 4269
Copper(II) sulfide, 4285
Europium(II) sulfide, 4293

Germanium(II) sulfide, 4419
Gold(III) sulfide, 0116
Iron disulfide, 4401
Iron(II) sulfide, 4400
Iron(III) sulfide, 4404
Manganese(II) sulfide, 4706
Manganese(IV) sulfide, 4707
Mercury(II) sulfide, 4607
Molybdenum(IV) sulfide, 4719
Potassium sulfide, 4670
Rhenium(VII) sulfide, 4891
Ruthenium(IV) sulfide, 4895
Samarium sulfide, 4899
Silver sulfide, 0026
Sodium disulfide, 4812
Sodium polysulfide, 4813
Sodium sulfide, 4811
Strontium sulfide, 4901
Tantalum(IV) sulfide, 4903
∗ Tetrakis(butylthio)uranium, 3731
∗ Thorium oxide sulfide, 4826
Tin(II) sulfide, 4900
Tin(IV) sulfide, 4902
Titanium(IV) sulfide, 4904
Uranium(IV) sulfide, 4905
∗ Zirconium oxide sulfide, 4827

METAL THIOCYANATES $M(SC{\equiv}N)_n$

Oxidants

1. von Schwartz, 1918, 299–300
2. *MCA Case History No. 853*

Metal thiocyanates are oxidised explosively by chlorates or nitrates when fused, or if intimately mixed, at 400°C or on spark or flame ignition [1]. Nitric acid violently oxidised an aqueous thiocyanate solution [2].

See Nitric acid: Metal thiocyanate
Sodium nitrite: Potassium thiocyanate

METATHESIS REACTIONS

Parkin, I.*Chem. & Ind.*, 1997, (18), 725

These are usually reactions of anhydrous transition and B metal halides with dry alkali metal salts such as the sulphides, nitrides, phosphides, arsenides etc. to give exchange of anions. They tend to be very exothermic with higher valence halides and are frequently initiated by mild warming or grinding. Metathesis is

described as a controlled explosion. Mixtures considered in the specific reference above include lithium nitride with tantalum pentachloride, titanium tetrachloride and vanadium tetrachloride, also barium nitride with manganese II iodide, the last reaction photographically illustrated.

See METAL PNICTIDES

MICROWAVE OVEN HEATING

1. Gedye, R. *et al., Tetrahedron Lett.*, 1986, **27**, 279–282
2. Watkins, K. W., *J. Chem. Educ.*, 1983, **60**, 1043
3. Bedson, A., *Chem. Brit.*, 1986, **23**, 894
4. Gadge, R. *et al., Educ. Chem.*, 1988, **25**(2), 55–56
5. Gilman, L. *et al., Anal. Chem.*, 1988, **60**, 1624–1625
6. Emsley, J., *New Scientist*, 1988, Nov. 12, 56–60
7. Anon., *Lab. News* (London), 31 Oct. 1988, (409), 2
8. Anon, *Safety Digest Univ. Safety Assoc.*, 1994, (50), 3
9. *Introduction to microwave sample preparation*, Kinston, H. M., Jassie, L. B. (eds.), ACS Professional Reference Ser., Washington, American Chemical Society, 1989
10. Anon., *Safety Digest Univ. Safety Assoc.*, 1992, **44**, 26

During an investigation of microwave oven heating on the oxidation of toluene by potassium permanganate in a sealed Teflon vessel, excessively high pressures developed and a violent explosion ensued [1]. The possibility of a second hazard, that of explosion of a flammable vapour in a microwave oven, had been foreseen previously [2]. The current state of development of microwave heating to speed up sample dissolution was reviewed [3]. Use of microwave ovens for rapid preparation of derivatives in sealed Teflon vessels for analytical purposes are discussed, and the need for caution to avoid explosions due to excessive solvent volumes is stressed [4]. The desirability of heating acid digestion mixtures, or indeed any liquid, by microwave heating in a sealed container without an adequate pressure relief device is questioned [5]. General aspects of microwave heating in chemical operations have been discussed [6]. A survey showed a large number of incidents, including 13 serious cases of scalding or oven doors being blown off, caused by misuse of microwave ovens and lack of precautions, largely among biologists [7]. A microwave oven was destroyed when agar jelly was (over)heated in a flask with (probably) a too tight stopper [8]. The new text book deals with preparation of mineral, metallic, biological and chemical samples, and safety aspects and precautions for the techniques [9]. Rupture of containers fitted with bursting discs, the bursting disc remaining undamaged, suggests that containers for microwave digestion of geological samples may not always be as strong as intended [10]. It should be noted that, with the foaming to be expected of a superheated liquid, vents would easily block even should a safety valve operate.

See also SAMPLE DISSOLUTION

DropBooks

MILD STEEL

MCA Case History No. 947

A small mild steel cylinder suitable for high pressure at ambient temperature was two-thirds filled with liquid ammonia by connecting it to a large ammonia cylinder and cooling the smaller cylinder to −70°C by immersion in a solid carbon dioxide–acetone bath. Some hours after filling, the cylinder burst, splitting cleanly along its length. This was caused by cryogenic embrittlement and weakening of the mild steel cylinder. Special alloys are required for operations at low temperatures and high pressures.

MILK POWDER

1. Buma, T. J. *et al., Chem. Abs.*, 1977, **87**, 83300
2. Anon, *Fire Prevention*, 1990, (228), 39
3. Anon., *Loss Prev. Bull.*, 1994, (119), 5.

Lumps of powdered milk formed near the hot-air inlet of spray driers may ignite spontaneously. The thermochemical mechanism has been investigated [1]. A case of probable spontaneous combustion in milk powder which had been accidentally wetted some weeks previously is described [2]. Following two explosions in a spray drier handling dairy products, investigation showed that milk powder, in air, showed exothermicity from 195°C. The drying air had been at 210°C, it was recommended that its temperature be reduced [3]. There are also carbon monoxide dangers in using alkaline cleaners on milk drying equipment without good ventilation

See also SUGARS

See other IGNITION SOURCES, AUTOIGNITION INCIDENTS

MINIMUM IGNITION ENERGY (MIE)

1. Nuzhda, L. I. *et al., Chem. Abs.*, 1984, **101**, 156838
2. Pratt, T. H., *Process Safety Progr.*, 1993, **12**(4), 203
3. Siwek, R. *et al., Process Safety Progr.*, 1995, **14**(2), 107

The MIE of gas — air or vapour — air mixtures can be determined from the structural formula and the molar heat of combustion of the compounds studied, and equations for the calculation are presented. The method is stated to give more accurate results than conventional methods used to assess flammability of mixtures of gas or vapour with air [1]. It is claimed that in oxygen MIEs are about a hundredfold lower than in air [2]. A study of the ignition behaviour of dusts, including correlation of electrical and mechanical minimum ignition spark energies and ignition temperature is made [3].

MISTS

1. Eichorn, P., *Petroleum Refiner*, 1955, **34**(11), 194
2. Kletz, T. A., *Process Safety Progress*, 1995, **14**(4), 273

Mists are dust clouds in which the particles happen to be liquid. Should that liquid be combustible, even though it is nowhere near its flash-point, explosion is possible.
See DUST EXPLOSION INCIDENTS

MIXING

1. Stuart, R. *et al.*, *Safety Digest Univ. Safety Assoc.*, 1993, **45**, 4
The safety, and the exact products, of reactions conducted at a significant scale can depend strongly upon the order and rate of mixing reagents and solvents. In general, the potential for full heat evolution or gas elimination should not be assembled until there is sufficient heat-sink, or vent, to control these. Reference [1] records a fatality which arose after alcohol was added to sodium, rather than sodium being added to excess alcohol, when disposing of surplus metal.
See also molybdenum nitride, AGITATION INCIDENTS

MOLECULAR SIEVE INCIDENTS

Air

Schoofs, G. R., *AIChE J.*, 1992, **38**(9), 1385
The larger size sieves preferentially absorb nitrogen from air and may therefore generate an oxygen enriched initial stream from large air-drying beds, when brought on line after regeneration. This increases fire risks if fuels be present. This phenomenon is not shown by 3A sieves, which are therefore to be preferred.
See OXYGEN ENRICHMENT

DropBooks

Ethylene

Doyle, W. H., *Loss Prev.*, 1969, **3**, 15
A 5A molecular sieve, not previously soaked in dilute ethylene, was used to dry compressed ethylene gas in a flow system. An exothermic reaction attained red heat and caused explosive failure of the dryer. The smaller-pored 3A sieve is not catalytically active towards ethylene.

Triaryl phosphates

Schmitt, C. R., *J. Fire Flamm.*, 1973, (4), 113–131
A molecular sieve bed was used to purify continuously the fire-resistant hydraulic fluid (a triaryl phosphate) in a large hydraulic press. Periodically the sieve bed was regenerated by treatment with steam, and then purified air at 205°C. After 9 years of uneventful operation, the bed ignited on admission of hot air. The fuel source was traced to the accumulation of organic residues (phenols or cresols?) on the sieve which were not removed by the steam/air treatment.

Other examples of molecular sieve incidents are:
Benzyl bromide, Molecular sieve, 2735
tert-Butyl hydroperoxide, Molecular sieves, 4477
Mercury(II) perchlorate · 6 (or 4)dimethyl sulfoxide, 4079

Nitromethane, Molecular sieve, 0456
Oxygen difluoride, Adsorbents, 4317
1,1,1-Trichloroethane, 0740

MOLTEN METAL EXPLOSIONS

1. Frölich, G., *Chem. Ing. Tech.*, 1978, **50**, 861–866
2. *Molten Metals and Water Explosions*, HSE Rept., London, HMSO, 1979
3. Vaughan, G. J., *Rept. SRD R177*, Warrington, UKAEA, 1980
4. Tso, C. P., PhD Thesis, University of California, Berkely, 1979
5. Mitin, V. P. *et al.*, *Chem. Abs.*, 1981, **94**, 88514
6. Shoji, S. *et al.*, *Bull. Jap. Soc. Mech. Eng.*, 1983, **26**, 791–796

Factors which determine whether or not there will be a vapour explosion when a hot melt (glass or various metals) comes into contact with water have been studied experimentally. Vapour generation must be preceeded by fragmentation of the melt to give enormous heat transfer coefficients [1]. This last report [2] in a series of 6 covers general aspects and precautions relevant to foundry practice, the earlier ones each dealing with specific metals and alloys. The molten metal–water explosion phenomenon has been reviewed with 130 references. [3]. A new thermal explosion model has been proposed and used to predict reaction zones in systems containing water and molten aluminium, lead and tin, among others [4]. The mechanisms of explosion when molten magnesium [5] or tin [6] contact water have been studied on the small scale. Other incidents of this type are:

SMELT
STEAM EXPLOSIONS
Aluminium, : Water (references 9,10), 0048
Copper, : Water, 4267
Tin, : Water (references 1–3), 4912

MOLTEN SALT BATHS

1. *Guidelines for Safety in Heat Treatment, I: Use of Molten Salt Baths*, Birmingham, University of Aston, 1984
2. Baum, R., *Chem. Eng. News*, 1982, **60**(41), 29
3. Anon., *CISHC Chem. Safety Summ.*, 1980, **51**, 75
4. *Precautions in the Use of Nitrate Salt Baths*, Min. of Labour, SHW booklet, London, HMSO, 1964
5. Pieters, 1957, 30
6. *Potential Hazards in the Use of Salt Baths for Heat Treatment of Metals*, NBFU Res. Rept. No. 2., New York, 1946
7. Beck, W., *Aluminium*, 1935, **17**, 3–6
8. Clark, E. R. *et al.*, *Chem. Abs.*, 1987, **107**, 119389

The most recent summary of the considerable hazards which may arise from incorrect use of molten salt baths and the materials in them covers all aspects of material storage, bath use, maintenance and cleaning, disposal of used materials and fire-fighting [1]. An account of a disastrous laboratory explosion caused by melting

together 1.3 kg of the oxidant sodium nitrite and 0.4 kg of the reducant potassium thiocyanate is remarkable in that it was claimed that the violent redox reaction on melting could not have been foreseen [2]. As well as for heat treatment, molten salt baths are also used to oxidise impurities from metal components. When filter plates excessively contaminated with polymer were lowered into the bath, an unusually fierce fire (possibly involving liberated oxygen) ensued [3].

The booklet covers hazards attendant on the use of molten nitrate salt baths for heat treatment of metals, including storage and disposal of salts, starting up, electrical heating, and emptying of salt baths. Readily oxidisable materials must be rigorously excluded from the vicinity of nitrate baths [4]. Earlier it had been reported that aluminium and its alloys if contaminated with organic matter may explode in nitrate–nitrite fused salt heating baths [5]. Uses, composition, and precautions in the use of molten salt baths are discussed. Most common causes of accidents are: steam explosions, trapping of air, explosive reactions with reducing metals (magnesium) and organic matter or cyanides from other heat treatment processes [6]. Explosions involving use of aluminium in nitrate baths have also been attributed to corrosive failure of the iron container, rather than to direct interaction with aluminium [7]. Heat treatment of aluminium–lithium and aluminium–magnesium alloys in nitrite–nitrate salt baths was studied [8].

See Sodium nitrite: Potassium thiocyanate

MOLTEN SALTS

Zhuchkov, P. A. *et al.*, *Chem. Abs.*, 1974, **80**, 28651

The causes of furnace blasts occurring in soda-regeneration plants when water is spilt into molten sodium carbonate, sodium chloride, sodium hydroxide, sodium sulfate or sodium sulfide are discussed, together with methods of prevention.

DropBooks

NATURAL FIBRES

See DUST EXPLOSION INCIDENTS (reference 15)

See Calcium oxide: Water (reference 3)
Potassium chlorate: Fabric, 4017
Nitric acid: Cellulose, 4436
Hydrogen peroxide: Acetic acid, Jute, 4477

See also COTTON

NEUTRALISATION INCIDENTS

Incidents of several different types have arisen from reactions involving neutralisation of an acid with a base where the exotherm (57.3 kJ/equivalent for strong acid–strong base reactions) has not occurred smoothly over an extended period, but has been sudden in effect for various reasons. Individually indexed neutralisation incidents are:

† Formaldehyde, : Magnesium carbonate hydroxide, 0416
Potassium hydroxide, : Acids, 4428

Sodium carbonate, 0552
Sulfuric acid, : Diethylamine, 4479
Sulfuric acid, : 4-Methylpyridine, 4479
2,4,6-Trichloro-1,3,5-triazine, : 2-Ethoxyethanol, 1038
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

NITRAMINE–METAL COMPLEXES $O_2NN \rightarrow M$

Palopali, S. F. *et al., Inorg. Chem.*, 1988, **27**, 2963–2971
Complexes of the explosively unstable nitramine ligands *N*-nitromethylamine (HL), *N,N′*-dinitrodiaminoethane (H_2L'), and 5-nitraminotetrazole (H_2L'') with ammine derivatives of divalent copper, nickel or palladium explode on heating or under a hammer blow. Compounds prepared were :

$Cu(NH_3)_2L_2$, $Cu(en)L_2$, $Cu(NH_3)_2L'$, $Ni(H_2O)_4L'$, $Ni(NH_3)_3L'$, $Pd(NH_3)_2L'$, $[Cu(en)_2]$ $\{[Cu(en)_2L'_2]_2\mu L'\}$.

Ligand bonding to metal was via O and/or N.

The individual ligands are:
N,N′-Dinitro-1,2-diaminoethane, 0916
5-*N*-Nitroaminotetrazole, 0415
N-Nitromethylamine, 0478
See other *N*-NITRO COMPOUNDS

NITRATING AGENTS

1. Dubar, J. *et al., Compt. rend. Ser. C*, 1968, **266**, 1114
2. Buckley, E. *et al., Chem. & Ind.*, 1978, 124–125
3. Feuer, H. *et al., J. Org. Chem.*, 1978, **43**, 4677

The potentially explosive character of various nitration mixtures (2-cyanopropyl nitrate in acetonitrile; solutions of dinitrogen tetraoxide in esters, ethers or hydrocarbons; dinitrogen pentaoxide in dichloromethane; nitronium tetrafluoroborate in sulfolane) are mentioned [1]. Use of mixtures of fuming nitric acid–sulfuric acid in acetic anhydride to highly nitrate naphthalene derivatives is accompanied by formation of tetranitromethane, and care is required [2]. When propyl nitrate is used as a nitrating agent, effective cooling at $-60^{\circ}C$ is necessary to deal with the highly exothermic reaction [3].

NITRATION INCIDENTS

1. Biasutti, 1974, 8, 123–125
2. Albright, Hanson, 1976
3. Obnovlenskii, P. A. *et al., Chem. Abs.*, 1975, **83**, 168135
4. Raczynski, S., *Chem. Abs.*, 1963, **59**, 15114e
5. Rüst, 1948, 317–319
6. Biasutti, 1981
7. Albright, M. F., in Kirk-Othmer, 1981, Vol. 15, 841–853

8. Evans, F. W. *et al.*, *Loss Prev. Safety Prom. Proc. Ind.*, 191–197, Frankfort, DECHEMA, 1978
9. Zeller, J. R., Paper 28, *ACS CHAS Div. Symp. Chem. Haz. Proc. Rev.*, 1984; Ch. 11 in *Chem. Proc. Haz. Rev.*, ACS Sympo. Ser. No. 274, 107–114, Washington, ACS, 1985
10. Sokhenko, V. I. *et al.*, *Chem. Abs.*, 1987, **107**, 9818
11. Sommer, E. *et al.*, *Proc. 7th Sympos. Chem. Probl. Stabil. Explos.*, 1986, 175–180
12. Wiss, J. *et al.*, *J. Loss Prevention*, 1955, **8**(4), 205
13. Wörsdörfer, U. *et al.*, *Prax. Sicherheitstech.* 1997, **4**, 355; *Chem. Abs.*, 1998, **128**, 77116m
14. Urben, P. G., *J. Chem. Educ.*, 1992, **69**, 334
15. Editor's comments, 1993

Accident statistics reveal nitration as the most widespread and powerfully destructive industrial unit process operation. This is because nitric acid can, under certain conditions, effect complete and highly exothermal conversion of organic molecules to gases, the reactions often being capable of acceleration to deflagration or detonation. Case histories are described and safety aspects of continuous nitration processes are discussed in detail [1]. Of the 25 chapters of the book [2], each a paper presented at the symposium on 'Advances in Industrial and Laboratory Nitrations' at Philadelphia in 1975, 3 deal with safety aspects of nitration: Ch. 8, Hanson, C. *et al.*, *Side Reactions during Aromatic Nitration*; Ch. 22, Biasutti, G. S., *Safe Manufacture and Handling of Liquid Nitric Esters*; Ch. 23, Brunberg, B., *Safe Manufacture and Handling of Liquid Nitric Esters: the Injector Nitration Process*

DropBooks

Reaction parameters important for control of continuous nitration systems were identified, as were secondary parameters useful for diagnostic/protective purposes. The algorithms developed were successfully applied to a pilot plant for continuous nitration of 2-pyridone in acetic anhydride [3]. Technological difficulties associated with methods of reducing explosion hazards in aromatic nitration were discussed [4], and many case histories of violent incidents during nitration operations have been collected [5,6]. In a comprehensive review, general safety precautions and information relevant to nitration are reported [7]. Safety considerations relevant to the development and design of a new industrial nitration plant are detailed [8]. An account is given of the relatively inexpensive methods used to develop safe processing and reaction conditions for the conversion of 5-chloro-1,3-dimethyl-1*H*-pyrazole to the 4-nitro derivative [9]. A detailed study of safety optimisation of aromatic nitration, with the particular example of chlorobenzene is reported in [12].

Use of sensors to measure gas phase NO_2 concentration, electrical conductivity of the reaction mass, and gas phase temperatures at several critical points in semi-continuous nitration reactors permits safe operation of nitration processes [10]. The use of non-aqueous titration analysis in the control of nitration processes in explosives manufacture is discussed [11].

Nitration is also a frequent cause of laboratory accident. A mixed acid nitration of arylcarboxylic esters, the substrate dissolved in sulphuric acid and nitric added

to this mix, was found to be increasingly thermally unstable with increasing nitric acid excess. Process safety could not be guaranteed with above 10% excess [13]. Some suggestions on safer, cleaner nitration procedures are given in [14]. There would be fewer laboratory nitration mishaps if reaction equations were written in full and balanced so that the usual reaction was seen as an acid catalysed dehydration of nitric acid, the supposed substrate being only a scavenger of the product of dehydration (and often also a base in the nitration environment). The competing radical oxidation reaction which is the direct cause of accident is not greatly acid catalysed, but autocatalytic and catalysed by free $\cdot NO_2$. Consideration of mechanism can usually produce safer procedures than scholastic labours in the academic literature, whereby methods are often inherited unchanged from the last century. It should be noted that most of the studies above come from the heavy chemical industry, who are economically constrained to use rather wet conditions (and nitration is a dehydration!) and commonly work with two phase mixtures. Their conclusions do not necessarily, or even usually, represent optimal laboratory procedure, especially for homogeneous nitrations [15].

Individually detailed nitration incidents are found under:
2-Chloro-1,3-dinitro-5-trifluoromethylbenzene, 2637
Dimethyl 4-acetamidophthalate: Nitric acid, 3520
4,6-Dinitro-1,3-benzenediol, 2198
Dinitrogen tetraoxide, Laboratory grease, 4747
2-Methyl-4-nitroimidazole, 1475
3-Methyl-4-nitropyridine *N*-oxide, 2317
Nitric acid, 4436
3-Nitroaniline: Nitric acid, Sulfuric acid, 2314
Nitronium perchlorate, 1,2-Epoxides, 4028
2,2′-Oxybis(ethyl nitrate), 3260
Sodium nitrate, Phenol, Trifluoroacetic acid, 4721
See also NITRATING AGENTS
See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

NITRIDES

There are three anions that may loosely claim to be nitrides. Pentazolides (salts of cyclic N_5^-) will all be explosive. Some azides (salts of N_3^-) fall just short of being explosive but all are violently unstable. The true nitrides, nominal derivatives of N^{3-}, are more various. In addition to some ionic structures, there are polymeric covalent examples, and some monomeric covalent ones, while most of those of transition metals are best considered as alloys. Several are endothermic and explosive, almost all are thermodynamically very unstable in air with respect to the oxide. Many are therefore pyrophoric if finely divided and also may react violently with water and, more particularly, acids, especially oxidising acids. A few are of considerable kinetic stability in these circumstances. There is no very clear classification of probable safety by position in the periodic table but polymeric and alloy structures are in general the more stable. Individual nitrides having entries:

* Ammonium nitridoosmate, 4523
Antimony(III) nitride, 4729
Barium nitride, 0219
* Barium nitridoosmate, 0213
Bismuth nitride, 0230
Cadmium nitride, 3960
Caesium nitride, 4266
Calcium nitride, 3946
* Carbonyl(pentasulfur pentanitrido)molybdenum, 0535
Cerium nitride, 3965
* Chloro-1,2,4-triselenadiazolium chloride, 4089
Chromium nitride, 4237
Cobalt(III) nitride, 4214
Copper(I) nitride, 4289
Diseleniumdisulfur tetranitride, 4769
Disulfur dinitride, 4754
Gold(I) nitride–ammonia, 0117
Gold(III) nitride trihydrate, 0118
* Iodinated poly(sulfur nitride), 4622
Lead nitride, 4753
Lithium nitride, 4688
Magnesium nitride, 4698
Mercury nitride, 4615
Molybdenum nitride (mixture of 3), 4714
Pentasulfur hexanitride, 4784
Plutonium nitride, 4726
* Poly(disilicon nitride), 4757
* Poly(selenium nitride), 4730
Poly(sulfur nitride), 4728
Potassium nitride, 4671
* Potassium nitridoosmate, 4651
Rhenium nitride tetrafluoride, 4344
Rubidium nitride, 4727
Silver nitride, 0038
* Silver trisulfurpentanitridate, 0024
Sodium nitride, 4723
* Sodium tetrasulfur pentanitridate, 4775
* Sodium tetrasulfur pentanitridate, 4775
Sodium trisulfurtrinitridate, 4760
Tetraselenium dinitride, 4756
* Tetraselenium tetranitride, 4771
* Tetratellurium tetranitride, 4773
* Tetratellurium tetranitride, 4773
Tetrasulfur dinitride, 4755
Tetrasulfur tetranitride, 4770
Thallium(I) nitride, 4731

DropBooks

Trifluorosulfur nitride, 4338
Trisilver tetranitride, 0040
Tritellurium tetranitride, 4772
Trithorium tetranitride, 4774
Uranium(III) nitride, 4732
Zirconium nitride, 4733

See Pentazole

See AZIDES, METAL PNICTIDES

NITRITE SALTS OF NITROGENOUS BASES $N^+ NO_2^-$

1. Mellor, 1940, Vol. 8, 289, 470–472
2. Ray, P. C. *et al., J. Chem. Soc.*, 1911, **99**, 1470; 1912, **101**, 141, 216

Ammonium and substituted-ammonium nitrite salts exhibit a range of instability, and reaction mixtures which may be expected to yield these products should be handled with care. Ammonium nitrite will decompose explosively either as the solid, or in conc. aqueous solution when heated to 60–70°C. Presence of traces of acid lowers the decomposition temperature markedly. Hydroxylammonium nitrite appears to be so unstable that it decomposes immediately in solution. Hydrazinium(1+) nitrite is a solid which explodes violently on percussion, or less vigorously if heated rapidly, and hydrogen azide may be a product of decomposition [1]. Mono- and di-alkylammonium nitrites decompose at temperatures below 60–70°C, but usually without violence [2]. Individual entries are:

Ammonium nitrite, 4521
Hydrazinium nitrite, 4548
Methylammonium nitrite, 0505

See other OXOSALTS OF NITROGENOUS BASES

NITROACYL HALIDES *o*-$O_2NArCO.Cl$, etc.

Aromatic acyl halides containing a nitro group adjacent to the halide function show a tendency towards violent thermal decomposition. The few individually indexed compounds are:

∗ 2,4-Dinitrobenzenesulfenyl chloride, 2099
2,4-Dinitrobenzenesulfonyl chloride, 2100
2,4-Dinitrophenylacetyl chloride, 2902
4-Hydroxy-3-nitrobenzenesulfonyl chloride, 2146
3-Methoxy-2-nitrobenzoyl chloride, 2915
4-Methoxy-3-nitrobenzoyl chloride, 2916
3-Methyl-2-nitrobenzoyl chloride, 2913
2-Nitrobenzoyl chloride, 2653
2-Nitrophenylacetyl chloride, 2914
4-Nitrothiophene-2-sulfonyl chloride, 1388

See other ACYL HALIDES

1. *Nitroparaffins*, TDS1, New York, Commercial Solvents Corp.,1968
2. Hass, H. B. *et al., Chem. Rev.*, 1943, **32**, 388
3. Noble, P. *et al., Chem. Rev.*, 1964, **64**, 20
4. Murray, S. B. *et al., Can. Pat. Appl.* 2123170, 1995

Nitromethane is a detonable explosive, nitroethane can be detonated if both hot and under strong confinement, other nitroalkanes are mild oxidants under ordinary conditions, but precautions should be taken when they are subjected to high temperatures and pressures, since violent reactions may occur [1]. Explosives are described consisting of nitromethane stabilised for transport by admixture with nitroethane or nitropropane, then resensitised by addition of an amine [4]. The polynitroalkanes, being more in oxygen balance than the mono-derivatives, tend to explode more easily [2], and caution is urged, particularly during distillation [3].

See also POLYNITROALKYL COMPOUNDS

Alkali metals, or Inorganic bases

Watts, C. E., *Chem. Eng. News*, 1952, **30**, 2344

Contact of nitroalkanes with inorganic bases must be effected under conditions which will avoid isolation in the dry state of the explosive metal salts of the isomeric *aci*-nitroparaffins.

Hopcalite

See HOPCALITE

Metal oxides

1. Hermoni, A. *et al., Chem. & Ind.*, 1960, 1265
2. Hermoni, A. *et al., Proc. 8th Combust. Symp.*, 1960, 1084–1088

DropBooks

Contact with metal oxides increases the sensitivity of nitromethane, nitroethane and 1-nitropropane to heat (and of nitromethane to detonation). Twenty-four oxides were examined in a simple quantitative test, and a mechanism was proposed. Cobalt, nickel, chromium, lead and silver oxides were the most effective in lowering ignition temperatures [1]. At 39 bar initial pressure, the catalytic decomposition by chromium or iron oxides becomes explosive at above 245°C [2].

Sodium or Potassium bicarbonate

Kirk-Othmer, 1996, Vol. 17, 216

Dry powder fire extinguishers containing bicarbonate should not be used on nitromethane or nitroethane.

See aci-NITRO SALTS, *C*-NITRO COMPOUNDS

Individually indexed compounds are:

- Aluminium chloride–nitromethane, 0063
- Chloronitromethane, 0396
- Ethyl 2-nitroethyl ether, 1662
- Nitroacetone, 1184

tert-Nitrobutane, 1660

Nitroethane, 0869

Nitromethane, 0456
∗ Nitrooximinomethane, 0409
1-Nitropropane, 1263
2-Nitropropane, 1264
∗ Potassium 1-nitroethane-1-oximate, 0756
∗ Tribromonitromethane, 0314
∗ Trichloronitromethane, 0331
∗ Tris(hydroxymethyl)nitromethane, 1664

NITROALKENES **$C{=}CNO_2$**

Several nitroalkenes show high reactivity and/or low stability, individually indexed compounds being:
∗ 3,3-Dimethyl-1-nitro-1-butyne, 2395
1,1-Dinitro-3-butene, 1508
2,3-Dinitro-2-butene, 1509
4-Fluoro-4,4-dinitrobutene, 1458
∗ 3-Methyl-4-nitro-1-buten-3-yl acetate, 2835
∗ 3-Methyl-4-nitro-2-buten-1-yl acetate, 2836
4-Nitro-1-butene, 1572
2-Nitropropene, 1183
Tetranitroethylene, 1010

NITROALKYL PEROXONITRATES **$O_2NC{-}COONO_2$**

See Dinitrogen tetraoxide: Cycloalkenes, etc.

NITROANILINES **O_2NArNH_2**

Chlorine (or other oxidant)

Hydrochloric acid
See Hydrogen chloride: Chlorine, Dinitroanilines

NITROAROMATIC–ALKALI HAZARDS

1. Merz, V. *et al.*, *Ber.*, 1871, **4**, 981–982
2. Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 389–390
3. (*MCA Data Sheets*); *Haz. Chem. Data*, 1975; *491M*, 1975
4. Bretherick, L., *Proc. 6th Int. Symp. Prev. Occ. Risks Chem. Ind.*, 539–546, Heidelberg, ISSA, 1979 (and additional bibliography)
5. Howes, R. J., private comm., 1979
6. Capellos, C. *et al.*, *Chem. Abs.*, 1982, **96**, 88003

It is widely stated in the usual reference texts that nitroaromatic compounds and more particularly polynitroaromatic compounds may present a severe explosion risk if subjected to shock, or if heated rapidly and uncontrollably, as in fire

situations. However, the same reference texts make no mention of the fact that there is also a risk of violent decomposition or explosion when nitroaromatic compounds are heated more moderately with caustic alkalies, even when water or organic solvents are also present. It was known more than 100 years ago that mononitroaromatics (nitro-benzene, -toluene, -naphthalene) would react violently on heating with caustic alkalies 'with generation of $1\frac{1}{2}$ foot flames', and that dinitro compounds were almost completely carbonised [1]. By 1914 the potential hazards involved in heating di- or tri-nitroaryl compounds with alkalies or ammonia were sufficiently well recognised for a general warning on the possibilities of violent or explosive reactions in such systems to have been published [2]. Knowledge of these potential hazards apparently had faded to the point where they were not mentioned in standard sources of information [3].

Several industrial explosions have occurred during the past 40 years which appear to be attributable to this cause, but here has been little recognition of this or of the common features in many of the incidents. Too little investigational work in this area has been published to allow any valid conclusions to be drawn as to the detailed course of the observed reactions. However, it may be more than coincidence that in all the incidents reported, the structures of the nitroaromatic compounds involved were such that *o*- or *p*-*aci*-nitroquinonoid salt species could have been formed under the reaction conditions. Many of these salts are of very limited thermal stability. All of the available (circumstantial) evidence was collected and published [4]. Limited work by DTA showed that *o*-nitrophenol and sodium hydroxide gave a sharp exotherm at 46°, and *p*-nitrophenol at 95°, while *m*-nitrophenol gave no significant evidence of reaction below 200°C. *o*-Nitroaniline gave a sharp exotherm at 217°, and *p*-nitroaniline at 246°C [5]. Electronic excitation of TNT leads to formation of *aci*-quinonoid transient intermediates, and action of various bases leads to deflagration of molten TNT [6].

DropBooks

Individually indexed incidents of this type are:
2-Chloro-4-nitrotoluene, : Sodium hydroxide, 2711
2,4-Dinitrotoluene, 2726
2,4-Dinitrotoluene, : Sodium oxide, 2726
Lithium 4-nitrothiophenoxide, 2177
4-Methyl-2-nitrophenol, 2767
2-Nitroanisole, : Sodium hydroxide, Zinc, 2768
Nitrobenzene, : Alkali, 2262
Sodium 2,4-dinitrophenoxide, 2115
Sodium 4-nitrophenoxide, 2183
Sodium 2-nitrothiophenoxide, 2182
2,4,5-Trinitrotoluene, 2702
See also *aci*-NITROQUINONOID COMPOUNDS, *C*-NITRO COMPOUNDS

NITROARYL COMPOUNDS **$ArNO_2$**

1. Chervin, S. *et al., Proc. Workshop Microcalorim. Energ. Mater.*, 1997, R1; *Chem. Abs.*, 1998, **129**, 262429z

This group covers aromatic nuclei bearing one nitro group; most mono-nitro benzenes can be persuaded to detonate by a tetryl booster; few are an immediate danger in the absence of other sources of energy. Calorimetric studies [1] suggest that nitroaryl compounds decompose by an autocatalytic mechanism, and thus stability may depend upon thermal history. Individually indexed compounds are:

4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3266
2-(2-Aminoethylamino)-5-methoxynitrobenzene, 3172
2-Amino-5-nitrophenol, 2316
∗ Amminebarium bis(nitrophenylide), 3518
1,3-Bis(trifluoromethyl)-5-nitrobenzene, 2885
3-Bromo-3(4-nitrophenyl)-3*H*-diazirine, 2645
N-Bromo-3-nitrophthalimide, 2884
tert-Butyl 4-nitroperoxybenzoate, 3400
4-Chloro-2,5-diethoxynitrobenzene, 3301
6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2102
N-Chloro-4-nitroaniline, 2231
2-Chloro-5-nitrobenzaldehyde, 2649
2-Chloro-6-nitrobenzaldehyde, 2650
4-Chloro-3-nitrobenzaldehyde, 2651
5-Chloro-2-nitrobenzaldehyde, 2652
2-Chloronitrobenzene, 2141
4-Chloronitrobenzene, 2142
2-Chloro-5-nitrobenzenesulfonic acid, 2144
2-Chloro-5-nitrobenzyl alcohol, 2715
4-Chloro-2-nitrobenzyl alcohol, 2716
4-Chloro-3-nitrobenzyl alcohol, 2717
5-Chloro-2-nitrobenzyl alcohol, 2718
6-Chloro-2-nitrobenzyl bromide, 2671
2-Chloro-4-nitrobenzyl chloride, 2678
4-Chloro-2-nitrobenzyl chloride, 2679
1-Chloro-4-(2-nitrophenyl)-2-butene, 3270
2-Chloro-4-nitrotoluene, 2711
4-Chloro-3-nitrotoluene, 2712
2-Cyano-4-nitrobenzenediazonium hydrogen sulfate, 2668
4-Cyano-3-nitrotoluene, 2917
2,6-Di-*tert*-butyl-4-nitrophenol, 3666
Dichloronitrobenzene, 2103
Diethyl 4-nitrophenyl phosphate, 3329
Diethyl 4-nitrophenyl thionophosphate, 3328
2,4-Difluoronitrobenzene, 2109
Dimethyl 4-acetamino-5-nitrophthalate, 3515
Disodium 4-nitrophenylphosphate, 2185
5-Fluoro-2-nitrophenol, 2167
3-Hydroxy-4-nitrobenzaldehyde, 2690
4-Hydroxy-3-nitrobenzaldehyde, 2691
5-Hydroxy-2-nitrobenzaldehyde, 2692

Lanthanum 2-nitrobenzoate, 3815
2-Methoxy-5-nitroaniline, 2802
3-Methoxy-2-nitrobenzaldehyde, 2937
3-Methoxy-2-nitrobenzoyldiazomethane, 3124
2-Methyl-5-nitroaniline, 2801
∗ *N*-Methyl-*p*-nitroanilinium 2(*N*-methyl-*N*-*p*-nitrophenylaminosulfonyl) ethylsulfate, 3713
3′-Methyl-2-nitrobenzanilide, 3645
2-Methyl-5-nitrobenzenesulfonic acid, 2772
4-Methyl-3-nitrobenzenesulfonic acid, 2773
2-Methyl-5-nitrobenzimidazole, 2940
∗ 2-Methyl-4-nitroimidazole, 1475
3-Methyl-4-nitrophenol, 2766
Nickel 2-nitrophenoxide, 3464
4-Nitroacetanilide, 2950
2-Nitroacetophenone, 2936
2-Nitroaniline, 2313
3-Nitroaniline, 2314
4-Nitroaniline, 2315
4-Nitroaniline-2-sulfonic acid, 2319
4-Nitroanilinium perchlorate, 2350
2-Nitroanisole, 2768
2-Nitrobenzaldehyde, 2686
3-Nitrobenzaldehyde, 2687
4-Nitrobenzaldehyde, 2688
Nitrobenzene, 2262
3-Nitrobenzenesulfonic acid, 2268
2-Nitrobenzoic acid, 2693
3-Nitrobenzoic acid, 2694
4-Nitrobenzoic acid, 2695
2-Nitrobenzonitrile, 2662
3-Nitrobenzoyl nitrate, 2664
2-Nitrobenzyl alcohol, 2769
3-Nitrobenzyl alcohol, 2770
4-Nitrobenzyl alcohol, 2771
2-Nitrobenzyl bromide, 2710
2-Nitrobenzyl chloride, 2713
4-Nitrobenzyl chloride, 2714
4-Nitrodiphenyl ether, 3472
mixo-Nitroindane, 3140
4-Nitroisopropylbenzene, 3157
Nitromesitylene, 3158
1-Nitronaphthalene, 3249
3-Nitroperchlorylbenzene, 2143
2-Nitrophenol, 2265
3-Nitrophenol, 2266

DropBooks

4-Nitrophenol, 2267
4-Nitrophenylacetic acid, 2938
3-Nitrophenylacetylene, 2905
N-(2-Nitrophenyl)-1,2-diaminoethane, 3001
3-(2-Nitrophenyl)-2-hydroxyiminopropanoic acid, 3131
1-(2-Nitrophenyl)-5-phenyltetrazole, 3602
4-Nitrophenylphosphorodichloridate, 2158
4-Nitrophenylpropan-2-one, 3142
2-Nitrophenylpropiolic acid, 3113
2-Nitrophenylsulfonyldiazomethane, 2700
3-Nitrophthalic acid, 2906
3-Nitropropiophenone, 3141
5-Nitrosalicylhydrazide, 2778
Nitroterephthalic acid, 2907
4-Nitrotoluene, 2764
mixo-Nitrotoluene, 2762
Potassium 4-nitrophenoxide, 2174
Scandium 3-nitrobenzoate, 3816
Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3505
Sodium 3-nitrobenzenesulfonate, 2184
5,10,15,20-Tetrakis(2-nitrophenyl)porphine, 3907
Thallium(I) 2- or 4-nitrophenoxide, 2186
Yttrium 4-nitrobenzoate trihydrate, 3817

See also LANTHANIDE METAL NITROBENZOATES, NITROALKANES, POLYNITROARYL COMPOUNDS

NITROARYLPHOSPHINIC ACIDS $O_2NArP(O)HOH$

Rowbotham, P. M. *et al.*, UK Pat. 2 048 883, 1980

These may be explosive under some conditions.

See other NITROARYL COMPOUNDS

NITROBENZALDEHYDES $O_2NC_6H_3(X)CO.H$

Cardillo, P. *et al., Proc. 5th Int. Sympos. Loss Prev. Saf. Prom. Process Ind.*, Cannes, Paper P16, 1–14, SCI (Paris), 1986

A series of 11 nitrobenzaldehydes was examined by TGA, DSC and ARC techniques. Only 5-hydroxy-2-nitrobenzaldehyde decomposed exothermally in an unsealed container, but all did so in sealed capsules, under dynamic, isothermal or adiabatic conditions, with evolution of much gas. Initial decomposition temperatures in °C (compound, ARC value, and DSC value at 10°/min, respectively, followed by ARC energy of decomposition in kJ/g) were:- 2-nitro-, 176, 220, 1.44; 3-nitro-, 166, 218, 1.94; 4-nitro-, 226, 260, 1.27; 2-chloro-5-nitro-, 156, 226, 697; 2-chloro-6-nitro-, 146, 220, .832; 4-chloro-3-nitro-, 116, 165, 1.42; 5-chloro-2-nitro-, 240, 3-hydroxy-4-nitro-, 200, 4-hydroxy-3-nitro-, 200, 5-hydroxy-2-nitro-, 175, 3-methoxy-4-nitrobenzaldehyde, 245°C, -. 4-Nitrobenzaldehyde showed by

far the highest self-heating rate in ARC tests (approaching 100°/min at 240°C) anf the final pressure exceeded 170 bar when the pressure relief operated. The results are compared with those from various nitrobenzyl derivatives.

Individually indexed compounds are:
2-Chloro-5-nitrobenzaldehyde, 2649
2-Chloro-6-nitrobenzaldehyde, 2650
4-Chloro-3-nitrobenzaldehyde, 2651
5-Chloro-2-nitrobenzaldehyde, 2652
3-Hydroxy-4-nitrobenzaldehyde, 2690
4-Hydroxy-3-nitrobenzaldehyde, 2691
5-Hydroxy-2-nitrobenzaldehyde, 2692
3-Methoxy-2-nitrobenzaldehyde, 2937
2-Nitrobenzaldehyde, 2686
3-Nitrobenzaldehyde, 2687
4-Nitrobenzaldehyde, 2688
See NITROBENZYL COMPOUNDS (next below)

NITROBENZYL COMPOUNDS $O_2NC_6H_4CH_2X$

1. Cardillo, P. *et al.*, *J. Chem. Eng. Data*, 1984, **29**, 348–351
2. Cardillo, P. *et al.*, *Proc. 5th Nat. Congr. Calorim. Therm. Anal.*, Trieste, 1983
3. Cardillo, P. *et al.*, *Proc. 15th Nat. Congr. Ital. Chem. Soc.*, 349–350, 1984; *Chim. e Ind.* (Milan), 1986, **68**(6), 68–70
4. Cardillo, P. *et al.*, *Chim. e Ind.* (Milan), 1985, **67**, 403–405

Thermal stabilities of the six *o*-, *m*- and *p*-nitrobenzyl bromides and chlorides were studied comparatively by TGA, DSC and ARC techniques. In open sample containers, only *o*-nitrobenzyl bromide decomposed exothermally, but in sealed capsules all the compounds decomposed exothermally after melting, with abundant gas evolution. The bromides were less stable than the chlorides, and *o*-isomers less stable than others. Very high self-heating rates (>10°C/min), pressure increase rates (20 bar/min) and final pressures (>170 bar, when relief valve opened) were observed for all samples in the ARC runs [1]. The effect of halogen substitution in the ring upon thermal stability of nitrobenzyl halides was studied by DTA, DSC and ARC techniques. The latter gave the following results for sealed bombs (onset of exotherm °C, maximum temperature °C and calculated energy of decomposition in kJ/g, respectively). 6-Chloro-2-nitrobenzyl bromide, 165, 306, 0.85; 4-chloro-2-nitrobenzyl chloride, 151, 230, 1.01. The bromide was the least stable, and above 190°C the self-heating rate (>10°/min) prevented adiabatic operation of the calorimeter, and the pressure very rapidly approached 130 bar [2]. ARC examination of some industrially important potentially thermally unstable nitrobenzyl alcohols gave the following results (onset of exothermic decomposition °C, final temperature °C and calculated energy of decomposition in kJ/g, repectively). 2-Nitrobenzyl alcohol, 201, 343, 1.78; 3-nitro, 221, 332, 1.32; 4-nitro, 236, 310, 0.93; 5-chloro-2-nitro, 191, 286, 1.15; 4-chloro-3-nitro, 211, 315, 1.15; 4-chloro-2-nitro, 201, 229, 1.19; 2-chloro-5-nitro, 211, 329, 1.38 [3]. ARC results for 2-chloro-4-nitrobenzyl chloride are 216, 261, 1.01 [4].

DropBooks

Individually indexed compounds are:
2-Chloro-5-nitrobenzyl alcohol, 2715
4-Chloro-2-nitrobenzyl alcohol, 2716
4-Chloro-3-nitrobenzyl alcohol, 2717
5-Chloro-2-nitrobenzyl alcohol, 2718
6-Chloro-2-nitrobenzyl bromide, 2671
2-Chloro-4-nitrobenzyl chloride, 2678
4-Chloro-2-nitrobenzyl chloride, 2679
2,6-Dinitrobenzyl bromide, 2672
2-Nitrobenzyl alcohol, 2769
3-Nitrobenzyl alcohol, 2770
4-Nitrobenzyl alcohol, 2771
2-Nitrobenzyl bromide, 2710
2-Nitrobenzyl chloride, 2713
4-Nitrobenzyl chloride, 2714
See other BENZYL COMPOUNDS

NITRO COMPOUNDS $C-NO_2$, $N-NO_2$

The presence of one or more nitro groups (with 69.6% oxygen) linked to C or N in an organic compound may have a significant effect on the reactivity, oxygen balance and stability of the compound. (Compounds with a nitro group linked to O, nitrate esters, are of very much lower stability and are dealt with separately). The class has been subdivided into the separately treated groups:

METAL NITROPHENOXIDES, NITROACYL HALIDES
NITROALKANES, NITROALKENES
NITROALKYL PEROXONITRATES, NITROARYL COMPOUNDS
NITROARYLPHOSPHINIC ACIDS, NITROBENZYL COMPOUNDS
C-NITRO COMPOUNDS, *N*-NITRO COMPOUNDS
aci-NITROQUINONOID COMPOUNDS, *aci*-NITRO SALTS
POLYNITROALKYL COMPOUNDS, POLYNITROARYL COMPOUNDS
POLYNITROAZOPYRIDINES

Other relevant entries are:

NITROAROMATIC–ALKALI HAZARDS

C-NITRO COMPOUNDS $C-NO_2$

1. Engelke, R. *et al., Int. J. Chem. Kinetics*, 1986, **18**, 1205
2. Constantinou, C. P., *Phil. Trans. R. Soc. London Ser. A*, 1992, **339**, 403

In general, *C*-nitro compounds are more stable than *N*-nitro compounds because of the higher bonding energies in the former type. Evidence is offered [1] that decomposition and explosion of many nitro-derivatives proceeds through the *aci*-form, and that sensitivity corresponds to the proportion of that present. In terms of this work, sensitisation by very small proportions of soluble organic bases is most important; this is not limited to nitroalkanes. TNT can apparently be brought to the sensitivity of lead azide by this means. For a physicist's view of this sensitisation,

see [2]. All but one of the separately treated groups named in the previous entry deal with *C*-nitro compounds, and some individually indexed compounds are:

2-Amino-4,6-dihydroxy-5-nitropyrimidine, 1436
2-Carbamoyl-2-nitroacetonitrile, 1116
5-Chloro-1,3-dimethyl-4-nitro-1*H*-pyrazole, 1864
Mercury(II) 5-nitrotetrazolide, 0981
1-Methylamino-1-methylthio-2-nitroethene, 1596
Methylnitrothiophene, 1850
Nitroacetaldehyde, 0763
2-Nitroethanol, 0871
2-Nitroethanonitrile, 0711
Nitromethane, 0456
5-Nitrotetrazole, 0387
3-Nitro-1,2,4-triazolone, 0716
Potassium 2,5-dinitrocyclopentanonide, 1847
Potassium 1-nitroethoxide, 0806
∗ Sodium diformylnitromethanide hydrate, 1076
Sodium 5-nitrotetrazolide, 0547

N-NITRO COMPOUNDS — N−NO_2

van Romburgh, P., *Chem. Weekblad*, 1934, **31**, 732–733

Many *N*-nitro compounds show explosive instability, arising from the low N−N bonding energy, and the explosive properties of *N*-alkyl-*N*-nitroarylamines have been discussed. Individually indexed compounds are:

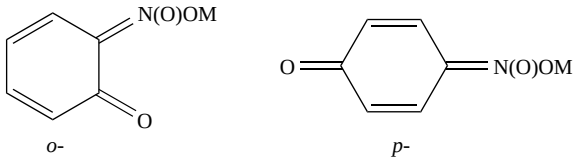
DropBooks

1-Amino-3-nitroguanidine, 0495
Ammonium 1,2-ethylenebis(nitramide), 0972
Azo-*N*-nitroformamidine, 0825
3,3′-Azo-(1-nitro-1,2,4-triazole), 1401
Bis(2-azidoethoxymethyl)nitramine, 2481
1,2-Bis(difluoroamino)-*N*-nitroethylamine, 0803
∗ Bis(2-nitratoethyl)nitric amide, 1602
N-Butyl-*N*-2-azidoethylnitramine, 2528
N,N′-Diacetyl-*N,N′*-dinitro-1,2-diaminoethane, 2426
1,12-Diazido-3,10-dioxa-5,8-dinitrazadodecane, 3049
1,3-Diazido-2-nitroazapropane, 0824
N,N′-Dimethyl-*N,N′*-dinitrooxamide, 1513
Dinitramine, 4442
N,N′-Dinitro-1,2-diaminoethane, 0916
1,3-Dinitro-2-imidazolidinone, 1142
N,N′-Dinitro-*N*-methyl-1,2-diaminoethane, 1276
N-Fluoro-*N*-nitrobutylamine, 1645
2-Hydroxy-4,6-bis(nitroamino)-1,3,5-triazine, 1122
Lead methylenebis(nitramide), 4882
Methylenebis(nitramine), 0483
Methylenebis(3-nitramino-4-methylfurazan), 2805

1-Methyl-3-nitroguanidinium nitrate, 0947
1-Methyl-3-nitroguanidinium perchlorate, 0939
1-Methyl-3-nitro-1-nitrosoguanidine, 0876
Nitric amide, 4471
2-(*N*-Nitroamino)pyridine *N*-oxide, 1851
4-(*N*-Nitroamino)pyridine *N*-oxide, 1852
5-*N*-Nitroaminotetrazole, 0415
1-Nitro-3-(2,4-dinitrophenyl)urea, 2705
Nitroguanidine, 0482
N-Nitromethanimine, 0408
N-Nitromethylamine, 0478
Nitrourea, 0460
Silver *N*-nitrosulfuric diamidate, 0016
N,2,3,5-Tetranitroaniline, 2121
N,2,4,6-Tetranitroaniline, 2123
N,2,4,6-Tetranitro-*N*-methylaniline, 2706
1,3,5,7-Tetranitroperhydro-1,3,5,7-tetrazocine, 1605
trans-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecahydronaphthalene, 2427
1,3,5-Trinitrohexahydro-1,3,5-triazine, 1219

See also *N*-AZOLIUM NITROIMIDATES

aci-NITROQUINONOID COMPOUNDS



o- *p*-

Generally, aromatic nitro compounds cannot form *aci*-nitro salts with bases unless there is an *o*- or *p*-substituent present (or is introduced by the action of the base) bearing a labile hydrogen atom. Then, isomerisation to produce *o*- or *p*-quinonoid *aci*-nitro species, then the salt, may be possible. Many salts of this type are unstable or explosive, and such species may have been involved in various incidents with nitro-aromatics and bases. Although more stable to acids than alkalis, nitroaromatic compounds, especially heterocyclic ones, are sometimes found to undergo vigorous decomposition on drying, which can be acid catalysed. Good washing is advisable before insertion in drying ovens. Individually indexed *aci*-nitro salts are:

∗ 1-Fluoro-2,4-dinitrobenzene, 2108
Lithium 4-nitrothiophenoxide, 2177
Potassium 4-methoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienonide, 2722
Potassium 6-*aci*-nitro-2,4-dinitro-2,4-cyclohexadieniminide, 2113
Potassium 6-*aci*-nitro-2,4-dinitro-1-phenylimino-2,4-cyclohexadienide, 3451
Potassium 4-nitrophenoxide, 2174
∗ Silver 4-nitrophenoxide, 2126

Sodium 1,4-bis(*aci*-nitro)-2,5-cyclohexadienide, 2188
Sodium 3,5-bis(*aci*-nitro)cyclohexene-4,6-diiminide, 2203
Sodium 4,4-dimethoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienide, 2951
Sodium 3-hydroxymercurio-2,6-dinitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2083
Sodium 2-hydroxymercurio-4-*aci*-nitro-2,5-cyclohexadienonide, 2171
Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2111
Sodium 6-*aci*-nitro-4-nitro-2,4-cyclohexadieniminide, 2200
Sodium 4-nitrophenoxide
Sodium 2-nitrothiophenoxide, 2182
2,4,6-Trinitrotoluene, : Potassium hydroxide, 2683
See NITROAROMATIC–ALKALI HAZARDS

aci-NITRO SALTS **−C=N(O)OM**

Many *aci*-nitro salts derived from action of bases on nitroalkanes are explosive in the dry state. Individually indexed compounds are:
Ammonium *aci*-nitromethanide, 0504
Dipotassium *aci*-nitroacetate, 0672
Mercury(II) *aci*-dinitromethanide, 0707
Nitromethane, : Lithium tetrahydroaluminate, 0456
∗ Potassium phenyldinitromethanide, 2682
∗ Sodium diformylnitromethanide hydrate, 1076
Sodium 1,3-dihydroxy-1,3-bis(*aci*-nitromethyl)-2,2,4,4-tetramethylcyclobutandiide, 3344
Thallium *aci*-phenylnitromethanide, 2723
See NITROALKANES: alkali metals, or inorganic bases
See also *aci*-NITROQUINONOID COMPOUNDS, (next above)

DropBooks

NITROSATED NYLON **$[-(CH_2)_mCO.N(N:O)(CH_2)_n-]_n$**

Anon., *ABCM Quart. Safety Summ.*, 1963, **34**, 20
Nylon, nitrosated with dinitrogen trioxide according to Belg. Pat. 606 944 and stored cold, exploded on being allowed to warm to ambient temperature. The *N*-nitroso nylon would be similar in structure to *N*-nitroso-*N*-alkylamides, some of which are thermally unstable. Nylon components should therefore be excluded from contact with nitrosating agents.
See other NITROSO COMPOUNDS

NITROSO ARENES **ArN:O**

Koikov, L. N. *et al.*, *J. Org. Chem. USSR*, 1985, **21**, 1564–1574
The general reaction of nitroso arenes with α-dimethylaminostyrenes in benzene or ether to produce $ArCO.C(NMe_2)=NC_6H_4R$ is vigorously exothermic, and with large quantities the reaction mixture may be ejected from the reaction vessel.
See NITROSO COMPOUNDS, (next below)

NITROSO COMPOUNDS C−N:O, N−N:O

A number of compounds containing nitroso or coordinated nitrosyl groups exhibit instability under appropriate conditions. Individually indexed compounds are:

Ammonium *N*-nitrosophenylaminooxide, 2399
N-(2-Chloroethyl)-*N*-nitrosocarbamoyl azide, 1131
1-Chloro-1-nitrosocyclohexane, 2419
2-Chloro-1-nitroso-2-phenylpropane, 3147
μ-Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino) titanium, 3028
N,N′-Dimethyl-*N,N′*-dinitrosooxamide, 1512
N,N′-Dimethyl-*N,N′*-dinitrosoterephthalamide, 3284
N,N-Dimethyl-4-nitrosoaniline, 2980
1,2-Dimethylnitrosohydrazine, 0946
3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, 1954
Dinitrosylnickel, 4741
Ethyl *N*-methyl-*N*-nitrosocarbamate, 1597
Lead(II) trinitrosobenzene-1,3,5-trioxide, 3594
1-Methyl-3-nitro-1-nitrosoguanidine, 0876
N-Methyl-*N*-nitrosourea, 0875
Nitritonitrosylnickel, 4742
N-Nitrosoacetanilide, 2949
Nitrosobenzene, 2261
N-Nitrosodiphenylamine, 3486
N-Nitrosoethyl-2-hydroxyethylamine, 1691
Nitrosoguanidine, 0481
N-Nitroso-6-hexanelactam, 2424
1-Nitroso-2-naphthol, 3250
2-Nitrosophenol, 2263
4-Nitrosophenol (1,4-Benzoquinone monoxime), 2264
Nitrosyl chloride, 4023
Nitrosyl cyanide, 0541
Nitrosylruthenium trichloride, 4144
Nitrosylsulfuric acid, 4438
Nitrosyl tetrafluorochlorate, 3985
Perfluoro-*tert*-nitrosobutane, 1370
∗ Potassium nitrosodisulfate, 4661
Sodium 4-nitrosophenoxide, 2181
1,3,5-Trinitrosohexahydro-1,3,5-triazine, 1217
Trinitrosophloroglucinol, 2117

See also NITROSO ARENES, NITROSATED NYLON, 3-NITROSOTRIAZENES

3-NITROSOTRIAZENES N=N−N(N:O)

Müller, E. *et al.*, *Chem. Ber.*, 1962, **95**, 1255

A very unstable series of compounds, many decomposing at well below 0°C. The products formed from *N*-sodio triazenes and nitrosyl chloride explode violently on

being disturbed with a wooden spatula, and are much more sensitive than those derived from silver triazenes. These exploded under a hammer-blow, or on friction from a metal spatula.

See other TRIAZENES

N−*O* COMPOUNDS N−O

There are a number of compounds containing N−O single bonds which are of limited or low stability. As well as the groups:

1,3,4-DIOXAZOLONES, FURAZAN N-OXIDES
HYDROXYLAMINIUM SALTS, ISOXAZOLES, 2H-1,2,4-OXADIAZOLO[2,3-a]PYRIDINE-2-THIONES
OXIMES, OXIME CARBAMATES

there are the individually indexed compounds:

3-Aminoisoxazole, 1136
5-Aminoisoxazole-3-carbonamide, 1476
4-Amino-3-isoxazolidinone, 1137
3-Amino-5-methylisoxazole, 1501
5-Amino-3-methylisoxazole, 1502
2-Amino-4-methyloxazole, 1500
5-Amino-3-methylthio-1,2,4-oxadiazole, 1192
Ammonium *N*-nitrosophenylaminooxide, 2399
2-Aza-1,3-dioxolanium perchlorate, 0898
Azoformaldoxime, 0815
Bis(1-benzo[*d*]triazolyl) carbonate, 3598
Bis(1-benzo[*d*]triazolyl) oxalate, 3629
Bis(trifluoromethyl) nitroxide, 0638
2-*tert*-Butyl-3-phenyloxaziridine, 3406
Calcium bis(*O*-hydroxylamide), 3930
Calcium hydroxide *O*-hydroxylamide, 3929
N-(Chlorocarbonyloxy)trimethylurea, 1924
2-Chloro-5-methylphenylhydroxylamine, 2796
2-Cyano-2-propyl nitrate, 1506
μ-Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino) titanium, 3028
3,4-Dichlorophenylhydroxylamine, 2243
Dicyanofurazan, 1803
3,4-Dimethyl-4-(3,4-dimethyl-5-isoxazolylazo)isoxazolin-5-one, 3309
3,5-Dimethylisoxazole, 1888
Dimethylthallium *N*-methylacetohydroxamate, 2008
O-(2,4-Dinitrophenyl)hydroxylamine, 2279
Disodium *N*,*N*′-dimethoxysulfonyldiamide, 0911
∗ 3-Ethyl-4-hydroxy-1,2,5-oxadiazole, 1504
2-Heptafluoropropyl-1,3,4-dioxazolone, 1812
1-Hydroxybenzotriazole, 2272

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4-Hydroxy-3,5-dimethyl-1,2,4-triazole, 1575
N-Hydroxydithiocarbamic acid, 0454
O-(2-Hydroxyethyl)hydroxylamine, 0944
1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0817
1-Hydroxyimidazole-2-carboxaldoxime 3-oxide, 1477
1-Hydroxyimidazole *N*-oxide, 1134
Hydroxylamine, 4498
N-Hydroxysuccinimide, 1469
Hydroxyurea
Hyponitrous acid, 4470
4-Iodo-3,5-dimethylisoxazole, 1868
† Isoxazole, 1110
Lead hyponitrite, 4745
Lithium sodium nitroxylate, 4683
Mercury(II) formohydroxamate, 0804
∗ *N*-Methoxy-*N*-methylbenzylidenimmonium methylsulfate, 3334
Methyl 4-bromobenzenediazoate, 2737
5-Methylisoxazole, 1468
† Methyl nitrite, 0455
† 2-Methyl-2-oxazoline, 1569
∗ *N*-(Methylphenylphosphinoyl)hydroxylamine, 2823
2-(4-Nitrophenoxyazo)benzoic acid, 3601
† Oxazole, 1111
2,2′-Oxybis(iminomethylfuran) mono-*N*-oxide, 3260
N-Phenylhydroxylamine, 2356
Phenylhydroxylaminium chloride, 2366
3-Phenyl-5-isoxazolone, 3122
∗ Potassium cyclohexanehexone 1,3,5-trioximate, 2625
Potassium hydroxylamine-*O*-sulfonate, 4458
∗ Potassium methanediazoate, 0449
Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, 4662
Potassium 1-phenylethanediazoate, 2964
Potassium *O*-propionohydroxamate, 1210
Silver benzo-1,2,3-triazole-1-oxide, 2127
∗ Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1409
∗ Sodium 4-chloroacetophenone oximate, 2927
∗ Sodium 3-methylisoxazolin-4,5-dione-4-oximate, 1419
Sodium nitroxylate, 4722
Sodium 3-phenylisoxazolin-4,5-dione-4-oximate, 3114
∗ Sodium tris(*O*,*O*′-1-oximatonaphthalene-1,2-dione)ferrate, 3871
Thallium(I) methanediazoate, 0458
N-Trifluoroacetoxy-2,4-dinitroaniline, 2892
N-Trimethylsilyl-*N*-trimethylsilyloxyacetoacetamide, 3375

NON-METAL AZIDES $E(N_3)_n$

This group contains compounds with azide groups linked to non-oxygenated non-metals, individually indexed compounds being:

∗ Aluminium tetraazidoborate, 0059
Ammonium azide, 4526
Azidodimethylborane, 0888
Azidoiodoiodonium hexafluoroantimonate, 4361
Azidosilane, 4501
Bis(trifluoromethyl) phosphorus(III) azide, 0639
∗ Boron azide dichloride, 0126
∗ Boron azide diiodide, 0148
Boron triazide, 0153
Diazidodichlorosilane, 4092
Diazidodimethylsilane, 0918
∗ Diphenyl azidophosphate, 3489
Diphenylphosphorus(III) azide, 3488
Disulfuryl diazide, 4780
1,1,3,3,5,5-Hexaazido-2,4,6-triaza-1,3,5-triphosphorine, 4795
Hydrazinium azide, 4550
Hydrogen azide, 4441
∗ Lithium tetraazidoborate, 0151
4-Nitrobenzenediazonium azide, 2209
Nitrosyl azide, 4766
∗ Phosphorus azide difluoride, 4315
∗ Phosphorus azide difluoride–borane, 4316
Phosphorus triazide, 4789
∗ Phosphorus triazide oxide, 4788
Silicon tetraazide, 4791
∗ Sodium hexaazidophosphate, 4794
Sulfinyl azide, 4778
Sulfuryl azide chloride, 4031
Sulfuryl diazide, 4779
∗ Tetramethylammonium diazidoiodate(I), 1750
Triazidoarsine, 0103
Triazidochlorosilane, 4035
† Trimethylsilyl azide

See related ACYL AZIDES, HALOGEN AZIDES

DropBooks

NON-METAL HALIDES AND THEIR OXIDES EX_n, EOX_n

This highly reactive class includes the separately treated groups:

HALOBORANES, *N*-HALOGEN COMPOUNDS
HALOPHOSPHINES, HALOSILANES
PERFLUOROSILANES

as well as the individually indexed compounds:

Arsenic pentafluoride, 0095
Arsenic trichloride, 0094
* Arsine–boron tribromide, 0101
Bis(*S*,*S*-difluoro-*N*-sulfimido)sulfur tetrafluoride, 4381
* Bis(trichlorophosphoranylidene)sulfamide, 4188
* Borane–phosphorus trifluoride, 0140
* Boron azide diiodide, 0148
Boron bromide diiodide, 0120
* Boron diiodophosphide, 0149
Boron tribromide, 0122
Boron trichloride, 0127
Boron trifluoride, 0129
* Boron trifluoride diethyl etherate, 1674
Boron triiodide, 0150
* *N*-Carboethoxyiminophosphoryl chloride, 1170
* *N*-Carbomethoxyiminophosphoryl chloride, 0743
Carbonyl dichloride, 0329
Chlorotetrafluorophosphorane, 3987
* Chloro-1,2,4-triselenadiazolium chloride, 4089
Diboron tetrachloride, 0161
Diboron tetrafluoride, 0162
* Dibromoborylphosphine, 0121
* Dichloroborane, 0124
* Dichlorodisilylaminoborane, 0125
* Diethylaminosulfur trifluoride, 1684
Diphosphoryl chloride, 4168
Diselenium dichloride, 4115
Disulfur dibromide, 0282
Disulfur dichloride, 4114
Disulfuryl dichloride, 4103
* Hexachlorocyclotriphosphazine, 4189
Hydriodic acid, 4423
Hydrogen bromide, 0247
Hydrogen chloride, 3993
Hydrogen fluoride, 4294
Krypton difluoride, 4313
* 4-Nitrophenylphosphorodichloridate, 2158
Nitrosyl fluoride, 4302
Nitryl fluoride, 4303
* Pentafluoroorthoselenic acid, 4354
* Phenylphosphonyl dichloride, 2245
* Phosphorus azide difluoride, 4315
* Phosphorus azide difluoride–borane, 4316
Phosphorus chloride difluoride, 3979
* Phosphorus diiodide triselenide, 4629

Phosphorus pentachloride, 4183
Phosphorus tribromide, 0293
Phosphorus trichloride, 4153
∗ Phosphorus tricyanide, 1343
Phosphorus trifluoride, 4339
Phosphorus triiodide, 4636
Phosphoryl chloride, 4149
∗ Phosphoryl dichloride isocyanate, 0327
∗ Poly(dibromosilylene), 0283
∗ Poly(difluorosilylene), 4330
∗ Potassium hexafluorosilicate(2−), 4364
Seleninyl bromide, 0275
Seleninyl chloride, 4097
Selenium difluoride dioxide, 4321
Selenium tetrabromide, 0295
Selenium tetrafluoride, 4351
∗ Silicon dibromide sulfide, 0281
Silicon tetrafluoride, 4352
Sulfinyl bromide, 0274
Sulfinyl chloride, 4096
Sulfinyl fluoride, 4318
Sulfonyl chloride, 4099
Sulfur dibromide, 0280
Sulfur dichloride, 4113
Sulfur hexafluoride, 4374
Sulfur tetrafluoride, 4350
Tellurium tetrachloride, 4175
∗ Tetracarbon monofluoride, 1362
Tetrachlorodiphosphane, 4171
Tetrachlorosilane, 4173
Tetraiododiphosphane, 4637
Thiazyl fluoride, 4306
∗ Thiophosphoryl chloride, 4154
∗ Thiophosphoryl chloride difluoride, 3980
∗ Thiophosphoryl fluoride, 4340
Thiotrithiazyl chloride, 4033
Triboron pentafluoride, 0175
∗ *B*-1,3,5-Trichloroborazine, 0174
1,3,5-Trichloro-2,4,6-trifluoroborazine, 0173
Trifluoromethanesulfinyl fluoride, 0354
∗ Trifluoroselenium hexafluoroarsenate, 0099
Trifluorosulfur nitride, 4338
Xenon difluoride, 4332
Xenon difluoride oxide, 4319
Xenon hexafluoride, 4377
Xenon tetrafluoride, 4353

DropBooks

NON-METAL HYDRIDES **EH_n**

Vogman, L. P., *Chem. Abs.*, 1984, **101**, 116147

The minimum oxygen concentration for explosion of most volatile hydrides of Group IIIA–VA elements is nearly zero, so complete exclusion of air or oxygen is essential for safe working. Presence of impurities in hydride mixtures further increases the danger of ignition.

There are separate group entries for:

BORANES, PHOSPHINES, SILANES

Most members of this readily oxidised class ignite in air, individually indexed compounds being:

† Ammonia, 4497
∗ Ammonium hydroxide, 4544
† Arsine, 0100
∗ Arsine–boron tribromide, 0101
∗ Borazine, 0176
∗ Cobalt tris(dihydrogenphosphide), 4203
∗ Dibromoborylphosphine, 0121
∗ Dichlorodisilylaminoborane, 0125
∗ 1,1-Diethoxy-1,3-disiladioxetane, 1762
† Hydrazine, 4520
Hydrogen bromide, 0247
Hydrogen chloride, 3993
† Hydrogen disulfide, 4484
Hydrogen fluoride, 4294
Hydrogen iodide
† Hydrogen selenide, 4486
† Hydrogen sulfide, 4483
† Hydrogen telluride, 4488
Hydrogen trisulfide, 4485
∗ Phospham, 4440
† Phosphine, 4508
'Solid Phosphorus hydride', 4449
Silicon monohydride, 4451
† Stibine, 4510
'Unsaturated' Silicon hydride, 4452

See related ALKYLNON-METAL HYDRIDES

NON-METAL OXIDES **E_mO_n**

The generally acidic materials in this group may function as oxidants, some rather powerful, under appropriate conditions. Individually indexed compounds are:

Arsenic pentaoxide, 0106
Arsenic trioxide, 0105
Boron trioxide, 0170
Carbon dioxide, 0557
† Carbon monoxide, 0555

† Carbonyl sulfide, 0556
Deuterium oxide, 4291
Diboron oxide, 0169
Dinitrogen oxide, 4744
Dinitrogen pentaoxide, 4748
Dinitrogen tetraoxide, 4747
Dinitrogen trioxide, 4746
∗ Diphenylselenone, 3494
Disulfur heptaoxide, 4870
Nitrogen dioxide, 4725
Nitrogen oxide, 4724
∗ Poly(dihydroxydioxodisilane), 4480
∗ Potassium hexaoxoxenonate–xenon trioxide, 4674
Selenium trioxide, 4852
Silicon dioxide, 4839
Silicon oxide, 4828
Sulfur dioxide, 4837
Sulfur trioxide, 4849
∗ Sulfur trioxide–dimethylformamide, 4850
Tellurium trioxide, 4853
∗ Tetrahydroxydioxotrisilane, 4536
Tetraphosphorus decaoxide, 4872
Tetraphosphorus hexaoxide, 4867
∗ Tetraphosphorus hexaoxide–bis(borane), 4868
∗ Tetraphosphorus hexaoxide tetrasulfide, 4869
∗ Tetraphosphorus tetraoxide trisulfide, 4859
Xenon(IV) hydroxide, 4533
Xenon tetraoxide, 4863
Xenon trioxide, 4857

See GRAPHITE OXIDE, HALOGEN OXIDES

DropBooks

NON-METAL PERCHLORATES $E(ClO_4)_n$

1. Solymosi, F., *Chem. Abs.*, 1972, **77**, 42498
2. Sunderlin, K. G. R., *Chem. Eng. News*, 1974, **52**(31), 3

The thermal stability, structures and physical properties of various non-metal perchlorates (nitrosyl, nitronium, hydrazinium, ammonium, etc.) have been reviewed [1]. Many organic perchlorates were examined for sensitivity to impact. The salts of cations containing only C, H and S exploded quite consistently, while those with C, H, and N, or C, H, N, and S did not explode, except 1,2-bis(ethylammonio)ethane diperchlorate [2].

Trifluoromethanesulfonic acid

Several perchlorate derivatives of non-metallic elements (including some non-nitrogenous organic compounds) are noted for explosive instability.

See Trifluoromethanesulfonic acid: Perchlorate salts
ALKENEBIS(SULFONIUM PERCHLORATES)
ORGANOSILYL PERCHLORATES
PERCHLORATE-DOPED CONDUCTING POLYMERS
PERCHLORATE SALTS OF NITROGENOUS BASES
and the individually indexed entries:
η-Benzenecyclopentadienyliron(II) perchlorate
1,3-Benzodithiolium perchlorate
∗ 1,1-Bis(dimethyl sulfoxide)telluracyclopentane diperchlorate, 1588
∗ Bis(triperchloratosilicon) oxide, 4190
Caesium tetraperchloratoiodate, 4161
1-Chloro-2,3-di(2-thienyl)cyclopropenium perchlorate, 3388
Chloronium perchlorate, 4065
4,4′-Diphenyl-2,2′-bi(1,3-dithiol)-2′-yl-2-ylium perchlorate, 3746
Diphenylcyclopropenylium perchlorate, 3680
1,3-Dithiolium perchlorate, 1094
Ferrocenium perchlorate, 3269
Fluoronium perchlorate, 3972
(Hydroxy)(oxo)(phenyl)-λ^3-iodanium perchlorate, 2299
Iodine(III) perchlorate, 4140
Nitronium perchlorate, 4028
Nitrosyl perchlorate, 4027
Nitryl perchlorate, 4029
∗ Peroxypropionyl perchlorate, 1167
Perylenium perchlorate, 3790
Phenyl, phenylethynyliodonium perchlorate, 3635
2-Tetrahydrofuranylidene(dimethylphenylphosphine-trimethylphosphine)-2,4,6-trimethylphenylnickel perchlorate, 3854
2-Tetrahydropyranylidene-bis(dimethylphenylphosphine)-3,4,6-trimethylphenylnickel perchlorate, 3877
2,3,4,6-Tetramethylpyrilium perchlorate, 3167
Tetraperchloratosilicon, 4169
Thianthrenium perchlorate, 3455
Thiotrithiazyl perchlorate, 4032
Triferrocenylcyclopropenium perchlorate, 3885
2,4,6-Trimethylpyrilium perchlorate, 2992
Trimethylsilyl perchlorate, 1302
2,4,6-Triphenylpyrilium perchlorate, 3839
Tris(ethylthio)cyclopropenium perchlorate, 3179
∗ 1,4,7-Trithia[7]ferrocenophene−acetonitrilecopper(I) perchlorate, 3710
Tropylium perchlorate, 2742
Xenon(II) fluoride perchlorate, 3977
See other PERCHLORATES

Some members of this group of elements are readily oxidised with more or less violence dependent upon the oxidant and conditions of contact. Individually indexed elements (and some binary compounds) are:

Argon, 0091
Arsenic, 0092
Boron, 0119
∗ Boron nitride, 0152
∗ Boron phosphide, 0156
Carbon, 0298
∗ Carbon tetraboride, 0309
† Hydrogen (Gas), 4453
† Hydrogen (Liquid), 4454
Nitrogen (Gas), 4734
Nitrogen (Liquid), 4735
Oxygen (Gas), 4831
Oxygen (Liquid), 4832
Ozone, 4846
† Phosphorus, 4874
∗ Selenium, 4908
∗ Silicon, 4909
† Sulfur, 4897
∗ Tellurium, 4916
Xenon, 4926

DropBooks

NON-METAL SULFIDES **E_mS_n**

In this group of readily oxidised materials, individually indexed compounds are:

Arsenic trisulfide, 0108
Bis(2,4-dinitrophenyl) disulfide, 3449
Bis(2-nitrophenyl) disulfide, 3465
Boron trisulfide, 0172
† Carbon disulfide, 0560
Carbon sulfide, 0559
† Carbonyl sulfide, 0556
∗ Disilyl sulfide, 4568
† Hydrogen disulfide, 4484
† Hydrogen selenide, 4486
† Hydrogen sulfide, 4483
Hydrogen trisulfide, 4485
∗ Phosphorus diiodide triselenide, 4629
Propadienedithione, 1350
∗ Silicon dibromide sulfide, 0281
Silicon monosulfide, 4898
Tetraarsenic tetrasulfide, 0109
∗ Tetramethyldiphosphane disulfide, 1766

Tetraphosphorus decasulfide, 4878
* Tetraphosphorus decasulfide . pyridine complex
* Tetraphosphorus hexaoxide tetrasulfide, 4869
* Tetraphosphorus tetraoxide trisulfide, 4859
* Tetraphosphorus triselenide, 4880
Tetraphosphorus trisulfide, 4877
* Tris(2-propylthio)phosphine

N–S COMPOUNDS N–S

1. Bojes, J. *et al.*, *Inorg. Synth.*, 1989, **25**, 30

Many compounds containing either single or multiple bonds between N and S show a considerable degree of instability. Information is given on hazards of, and precautions in handling derivatives of cyclic N−S compounds [1]. Individually indexed compounds are:

Amidosulfuric acid, 4499
5-Amino-1,2,3,4-thiatriazole, 0413
* Ammonium amidoselenate, 4557
Ammonium amidosulfate, 4556
* Ammonium thiosulfate, 4573
* Ammonium 2,4,6-tris(dioxoselena)hexahydrotriazine-1,3,5-triide
Benzo-1,2,3-thiadiazole, 2199
Benzo-1,2,3-thiadiazole 1,1-dioxide, 2191
Bis(*S*,*S*-difluoro-*N*-sulfimido)sulfur tetrafluoride, 4381
Bis(dimethylamino) sulfoxide, 1757
Bis-*N*(imidosulfurdifluoridato)mercury, 4342
3,4-Bis(1,2,3,4-thiatriazol-5-ylthio)maleimide, 2073
Bis(1,2,3,4-thiatriazol-5-ylthio)methane, 1084
* Bis(trichlorophosphoranylidene)sulfamide, 4188
* Carbonyl(pentasulfur pentanitrido)molybdenum, 0535
(Chlorocarbonyl)imidosulfur difluoride, 0318
* Chlorosulfonyl isocyanate, 0324
5-Chloro-1,2,3-thiadiazole, 0655
* Chloro-1,2,4-triselenadiazolium chloride, 4089
Cyclopentaazathienium chloride, 4034
1-(4-Diazoniophenyl)-1,2-dihydropyridine-2-iminosulfinate, 3392
N,N-Dichloropentafluorosulfanylamine, 4060
S-Diethylamino(methylimino)sulfur(IV) fluoride
Diethylaminosulfinyl chloride, 1679
Diethylaminosulfur trifluoride, 1684
S,*S*-Dimethylpentasulfur hexanitride, 3647
* 2,2-Diphenyl-1,3,4-thiadiazoline, 3647
Disulfur dinitride, 4754
* Disulfur thiocyanate, 1003
Ethyl 4-bromo-1,1,3-trioxoisothiazoleacetate, 2792
Ethyl 6-ethoxycarbonyl-3,4-dihydro-1,1,3-trioxo-2-pyrazolo[3,4-d]
isothiazole-2-acetate, 3403

N-Fluoroiminosulfur tetrafluoride, 4357
5-Hydrazino-1,2,3,4-thiatriazole, 0462
Iodinated poly(sulfur nitride), 4622
Mercury(I) thionitrosylate, 4610
4-Morpholinesulfenyl chloride, 1586
4,4′-Oxybis(benzenesulfonylhydrazide), 3525
Pentamethylcyclopentadienyl-bis(thiolatothiatriazyl)rhodium, 3534
Pentasulfur hexanitride, 4784
N-Phenyl-1,2,3,4-thiatriazolamine, 2729
∗ Poly(selenium nitride), 4730
Poly(sulfur nitride), 4728
∗ Potassium azodisulfonate, 4663
Potassium 4-nitrobenzeneazosulfonate, 2175
Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, 4662
Potassium sulfurdiimidate, 4664
Potassium thiazate, 4648
5-(Prop-2-ynyloxy)-1,2,3,4-thiatriazole, 1420
∗ Seleninyl bis(dimethylamide), 1758
Silver trisulfurpentanitridate, 0024
Sodium tetrasulfur pentanitridate, 4775
Sodium trisulfurtrinitridate, 4760
Sulfinylcyanamide, 0542
Sulfur oxide-(*N*-fluorosulfonyl)imide, 4305
∗ Sulfur thiocyanate, 1002
∗ Tetraselenium dinitride, 4756
∗ Tetraselenium tetranitride, 4771
Tetrasulfur dinitride, 4755
∗ Tetrasulfurtetraimide–silver perchlorate, 0029
Tetrasulfur tetranitride, 4770
∗ Tetratellurium tetranitride, 4773
Thiazyl fluoride, 4306
Thiotrithiazyl chloride, 4033
Thiotrithiazyl nitrate, 4767
Thiotrithiazyl perchlorate, 4032
2-Thioxo-4-thiazolidinone, 1112
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazine, 4145
1,3,5-Trichlorotrithiahexahydro-1,3,5-triazinemolybdenum, 4142
N-(Trifluoromethylsulfinyl)trifluoromethylimidosulfinyl azide, 0640
Trifluorosulfur nitride, 4338
Tris(thionitrosyl)thallium, 4764
See also *N* -HALOGEN COMPOUNDS

DropBooks

NUCLEAR WASTES

1. MacIlwhain., C. *Nature*, 1996, **383**(6599), 21
2. MacKenzie, D., *New Scientist*, 1993, (1869), 6; *ibid.*, 1993, (1870), 5

3. Scheele, R. D. *et al., Chem. Abs., 1993,* **119**, 262597a
4. Ashby, E. C. *et al., J. Amer. Chem. Soc.*, 1993, **115**, 1171
5. Silva, M., *Nucl. Saf.*, 1992, **33**(2), 220
6. Anon., *Chem. Eng. News*, 1993, **71**(51), 14
7. Hyder, M. L., *Nucl. Technol.*, 1996, **116**(3), 327
8. Johnson, J., *Chem. Eng. News*, 1997, **75**(31), 10

There are chemical explosion hazards associated with stored reprocessing residues. The explosion near Chelyabinsk in the Urals in 1958 was, it has been suggested, powered by interaction of sodium nitrate and/or nitric acid with sodium acetate/acetic acid in nitrate wastes neutralised with sodium acetate, then stored and allowed to concentrate by radioactive heating [1]. A reprocessing incident at Tomsk in 1993 was apparently caused by adding nitric acid to an inadequately stirred tank of actinide salts, mostly uranium, with a butyl phosphate/paraffin extraction solvent. The substantial explosion was probably caused by nitric acid oxidation of the organics [2]. Explosive 'red oils', apparently organic nitrate by-products, are a hazard of such processing [6]. Experiment shows that, when heated above 160°C with nitric acid or metal nitrates, (tri)butyl phosphate generates gas mixtures which can autoignite. Pressures of tens of bars may be generated. It is suggested that this mechanism explains some reprocessing explosions [7]. A study of the risks with nitrate residues containing ferrocyanide as fuel has been published [3]. Explosions from extremely prolonged storage of nitric acid and hydroxylamine solutions, with and without hydrazine, which are used as reagents in reprocessing are also reported. Initial concentration by evaporation seems to be involved [8].

Gas evolution, by radiation induced dissociation of water and other components, can also permit build-up of pressure behind crusts forming on evaporation of solvent; should the hydrogen peroxide also formed from water later decompose, the gas produced could be an explosive mixture of hydrogen and oxygen. Alkaline reprocessing wastes containing ethylenediamine tetracetic acid (EDTA) evolve large volumes of hydrogen. It is postulated that this is by radiation cleavage of EDTA to formaldehyde, which is shown to produce hydrogen chemically when at low concentrations in aqueous alkali [4].

For a general consideration of largely chemical reaction hazards of concentrated wastes [5].

See Formaldehyde, Nitric acid

See also IRRADIATION DECOMPOSITION INCIDENTS

OLEUM (FUMING SULFURIC ACID) $H_2SO_4.SO_3$

See Sulfur trioxide: Sulfuric acid

ORGANIC ACIDS RCO.OH, $ArSO_2$.OH, ArOH, etc.

This group has examples of many types of acids derived from aliphatic, aromatic and heterocyclic radicals, with carboxylic, phenolic or sulfonic or related functional substituents. Individually indexed acids are:

Acetic acid, 0833
Acetylenedicarboxylic acid, 1405
O-Acetylsalicylic acid, 3137
1-Acetyl-4-(4′-sulfophenyl)-3-tetrazene, 2982
Acrylic acid, 1148
Adipic acid, 2441
Azelaic acid, 3187
Azidoacetic acid, 0774
Azidodithioformic acid, 0386
Benzeneseleninic acid, 2335
Benzeneselenonic acid, 2338
Benzoic acid, 2732
Bis(3-carboxypropionyl) peroxide, 2990
4-Bromomethylbenzoic acid, 2926
Butyric acid, 1614
∗ 2-Carboxy-3,6-dimethylbenzenediazonium chloride, 3138
∗ *S*-Carboxymethylisothiouronium chloride, 1245
2-Chloro-5-nitrobenzenesulfonic acid, 2144
Citric acid, 2389
Citronellic acid, 3352
Cyanoacetic acid, 1113
Diazirine-3,3-dicarboxylic acid, 1080
Diazomalonic acid, 1081
2,2-Dibromo-1,3-dimethylcyclopropanoic acid, 2364
N,N-Dichloroglycine, 0739
Difluoroacetic acid, 0702
Dihydroxymaleic acid, 1447
3,5-Dimethylbenzoic acid, 3152
2,5-Dinitro-3-methylbenzoic acid, 2919
∗ Ferrocene-1,1′-dicarboxylic acid, 3479
Formic acid, 4885
Fumaric acid, 1446
Glyoxylic acid, 0724
2,4-Hexadienoic acid, 2385
2,4-Hexadiyne-1,6-dioic acid, 2094
4-Hydroxy-*trans*-cinnamic acid, 3136
4-Hydroxy-3,5-dinitrobenzenearsonic acid, 2220
N-Hydroxydithiocarbamic acid, 0454
1-Hydroxyethylidene-1,1-diphosphonic acid, 0956
2-Hydroxy-2-methylglutaric acid, 2445
2-Iodylbenzoic acid
Lactic acid, 1234
Methacrylic acid, 1530
Methanesulfonic acid, 0488
2-Methyl-5-nitrobenzenesulfonic acid, 2772
4-Methyl-3-nitrobenzenesulfonic acid, 2773

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4-Nitroaniline-2-sulfonic acid, 2319
3-Nitrobenzenesulfonic acid, 2268
2-Nitrobenzoic acid, 2693
3-Nitrobenzoic acid, 2694
4-Nitrobenzoic acid, 2695
2-(4-Nitrophenoxyazo)benzoic acid, 3601
∗ 3-(2-Nitrophenyl) -2-hydroxyiminopropanoic acid, 3131
2-Nitrophenylpropiolic acid, 3113
3-Nitrophthalic acid, 2906
Nitroterephthalic acid, 2907
9,12,15-Octadecatrienoic acid, 3771
cis-9-Octadecenoic acid, 3774
Octatetrayne-1,8-dicarboxylic acid, 3235
Oxalic acid, 0725
Pentanesulfonic acid, 2020
Perfluorosuccinic acid, 1391
3-Peroxycamphoric acid, 3348
Phthalic acid, 2923
Picric acid, 2118
∗ Potassium hydrogen acetylenedicarboxylate, 1382
∗ Potassium hydrogen tartrate, 1462
E-Propene-1,2,3-tricarboxylic acid, 2342
Propiolic acid, 1086
2,5-Pyridinedicarboxylic acid, 2696
Pyruvic acid, 1150
Tartaric acid, 1545
Terephthalic acid, 2924
† Thiolacetic acid, 0832
4-Toluenesulfonic acid, 2808
Trichloroacetic acid, 0658
Trifluoroacetic acid, 0665
Trifluoromethanesulfonic acid, 0375
Trinitroresorcinol, 2119

ORGANIC AZIDES RN_3, ArN_3

1. Boyer, J. H. *et al., J. Chem. Eng. Data*, 1964, **9**, 480; *Chem. Eng. News*, 1964, **42**(31), 6
2. Draper, R. W., *J. Chem. Soc., Perkin Trans. I*, 1983, 2787
3. Scheri, S. H. *et al., J. Mol. Struct.*, 1986, **14** 7, 203–204
4. Petrie M. A. *et al., J. Amer. Chem. Soc.*, 1997, **119**, 8802

The need for careful and small-scale handling of organic azides, which are usually heat- or shock-sensitive compounds of varying degrees of stability, sensitive to traces of strong acids and metallic salts which may catalyse explosive decomposition, has been discussed. The presence of more than one azido group, particularly if on the same atom (C or N), greatly reduces the stability [1]. Two reaction systems used to prepare steroidal azides are potentially dangerous, and should only be used

with extensive safety precautions. The first involves use of chromium trioxide, sodium azide and acetic acid, and is likely to produce chromyl azide and hydrazoic acid, both explosive. The second uses lead(IV) acetate and trimethylsilyl azide and could produce lead azide. Use of remote control handling equipment is recommended [2]. Unsaturated azides containing one or more double or triple bonds, and one or more azide groups, are particularly dangerous, and should be handled with the utmost care [3]. Not surprisingly, all salts of the triazido carbenium ion (N_9C+) were found to be sensitve explosives, the perchlorate was the most sensitive, the dinitramide the most powerful [4].

This class contains the separately treated groups:

See also ACYL AZIDES, 2-AZIDOCARBONYL COMPOUNDS

as well as the individually indexed compounds:

Azidoacetonitrile, 0714
Azidoacetyl chloride, 0693
4-Azidobenzaldehyde, 2697
7-Azidobicyclo[2.2.1]hepta-2,5-diene, 2777
Azido-2-butyne, 1473
2-*trans*-1-Azido-1,2-dihydroacenaphthyl nitrate, 3466
∗ *N*-Azidodimethylamine, 0915
4-Azido-*N,N*-dimethylaniline, 3331
2-Azido-3,5-dinitrofuran, 1384
2-Azidoethanol, 0873
6-Azidohexyl 6-azidohexanoate, 3551
2-Azidomethylbenzenediazonium tetrafluoroborate, 2708
2-Azidoperfluoronaphthalene, 3234
2-Azido-2-phenylpropane, 3159
3-Azidopropene, 1188
3-Azidopropyne, 1114
5-Azidotetrazole, 0388
3-Azido-1,2,4-triazole, 0717
Benzyl azide, 2779
∗ Bis(2-azidobenzoyl) peroxide, 3628
1,2-Bis(2-azidoethoxy)ethane, 2479
Bis(2-azidoethoxymethyl)nitramine, 2481
3,3-Bis(azidomethyl)oxetane, 1902
N-Butyl-*N*-2-azidoethylnitramine, 2528
1,3-Diazidobenzene, 2207
1,4-Diazidobenzene, 2208
2,3-Diazido-1,3-butadiene, 1437
2,4-Diazido-6-dimethylamino-1,3,5-triazine, 1876
1,12-Diazido-3,10-dioxa-5,8-dinitrazadodecane, 3049
1,1-Diazidoethane, 0818
1,2-Diazidoethane, 0819
Diazidomalononitrile, 1347
Diazidomethane, 0414

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Diazidomethyleneazine, 1021
Diazidomethylenecyanamide, 1017
1,3-Diazido-2-nitroazapropane, 0824
1,1-Diazidophenylethane, 2953
1,2-Diazido-1-phenylethane, 2954
2,2-Diazidopropane, 1216
1,3-Diazidopropene, 1143
2,3-Diazidopropiononitrile, 1121
2,6-Diazidopyrazine, 1400
3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2403
Ethyl azide, 0872
Ethyl 2,3-diazidopropionate, 1903
∗ 1-Ferrocenyl-2-methylpropyl azide, 3661
Glycidyl azide, 1191
Fluorodinitromethyl azide, 0341
Methyl azide, 0459
Methyl 2-azidobenzoate, 2939
Methyl 3,3-diazido-2-cyanoacrylate, 1824
1,1′-Oxybis-2-azidoethane, 1604
Phenyl azide, 2271
Phenyldiazidomethane, 2730
2,2′-[1,4-Phenylenebis(azidomethylidyne)]bis(propanedinitrile), 3622
I-Phenyl-*I*-(*p*-toluenesulfonyloxy)-(2-azido-2-phenyl)vinyliodine(III)
Picryl azide, 2092
Silver 2-azido-4,6-dinitrophenoxide, 2075
∗ Thiocarbonyl azide thiocyanate, 1011
1,1,1-Triazidodinitroethane, 0683
Triazidomethane, 0389
∗ Triazidomethylium hexachloroantimonate, 0335
2,4,6-Triazido-1,3,5-triazine, 1348
Trifluoromethyl azide, 0347
Triphenylmethyl azide, 3783
Tris(2-azidoethyl)amine, 2482
1,1,1-Tris(azidomethyl)ethane, 1937
Vinyl azide, 0770

See related NON-METAL AZIDES

ORGANIC BASES

The separately treated METAL ALKOXIDES may perhaps be regarded as organic bases, as well as the more conventional nitrogenous bases below:

Aminoguanidine, 0507
1-Amino-2-propanol, 1311
Benzylamine, 2812
Benzyldimethylamine, 3168
Bis(2-aminoethyl)amine, 1777

N,*N*′-Bis(2-aminoethyl)1,2-diaminoethane, 2599
† 1,2-Bis(dimethylamino)ethane, 2579
Bis(2-fluoro-2,2-dinitroethyl)amine, 1459
† Butylamine, 1723
† 2-Butylamine, 1724
† Butylethylamine, 2565
† Cyclohexylamine, 2521
† Cyclopentylamine, 1991
† Diallylamine, 2450
1,4-Diaminobenzene, 2371
1,2-Diaminoethane, 0953
† 1,2-Diaminopropane, 1325
† 1,3-Diaminopropane, 1326
1,11-Diamino-3,6,9-triazaundecane, 3101
1,4-Diazabicyclo[2.2.2]octane, 2473
Dibutylamine, 3083
† Di-2-butylamine, 3084
3-Dibutylaminopropylamine, 3416
† Diethylamine, 1726
3-Diethylaminopropylamine, 2877
† Diisobutylamine, 3085
† Diisopropylamine, 2566
3,3′-Dimethoxy-4,4′-diaminobiphenyl, 3660
† Dimethylamine, 0941
(Dimethylamino)acetylene, 1564
† 2-Dimethylaminoethylamine, 1755
N,*N*-Dimethylaniline, 2993
† 1,3-Dimethylbutylamine, 2567
† 1,2-Dimethylhydrazine, 0955
† 2,6-Dimethylpiperidine, 2868
† 1,1-Dimethylpropylamine, 2028
† 1,2-Dimethylpropylamine, 2029
† 2,2-Dimethylpropylamine, 2030
† *N*, *N*-Dimethylpropylamine, 2301
† Dipropylamine, 2568
† Ethylamine, 0942
† Ethyldimethylamine, 1727
5-Ethyl-2-methylpyridine, 2995
† 1-Ethylpiperidine, 2869
† 2-Ethylpiperidine, 2870
Hexamethylenetetramine, 2477
2-Hydroxyethylamine, 0943
N-2-Hydroxyethyl-1,2-diaminoethane, 1756
N-2-Hydroxyethyldimethylamine, 1729
† Isobutylamine, 1728
† Isopentylamine, 2032

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† Isopropylamine, 1308
† Methylamine, 0493
† *N*-Methylbutylamine, 2033
† Methylhydrazine, 0503
† 4-Methylmorpholine, 1995
† 1-Methylpiperidine, 2522
† 2-Methylpiperidine, 2523
† 3-Methylpiperidine, 2524
† 4-Methylpiperidine, 2525
2-Methylpyridine, 2355
† *N*-Methylpyrrolidine, 1992
Morpholine, 1657
† Pentylamine, 2034
† Perhydroazepine, 2526
Phenylhydrazine, 2373
N-Phenylhydroxylamine, 2356
Piperazine, 1689
† Piperidine, 1993
† Propylamine, 1309
† Pyridine, 1848
Quinoline, 3121
† 1,2,3,6-Tetrahydropyridine, 1930
1,3,4,7-Tetramethylisoindole, 3528
1,2,4,5-Tetrazine, 0715
Thiourea, 0480
3,6,9-Triaza-11-aminoundecanol, 3100
1,3,5-Triazine, 1115
† Triethylamine, 2569
† Trimethylamine, 1310
2,4,6-Tris(dimethylaminomethyl)phenol, 3694
Tris(hydroxymethyl)methylamine, 1731
Urea, 0475
Vinylpyridine, 2759

ORGANIC ISOCYANATES **RN═C═O**

1. Mumford, C. J. *et al., Loss Prev. Bull.*, 1991, **102**, 7

These high energy species are extremely reactive, with themselves and with nucleophiles, and can generate runaway exotherms. With water, rapid evolution of carbon dioxide results. Some instances are reported [1]. A compound of this class was resposible for the worst chemical industry accident to date. Di-isocyanates are extensively employed, with polyols, to generate polyurethane polymers. The polymerisation temperature should be held below 180°C or decomposition may occur which, in the case of foams, may induce later autoignition.

Individually indexed compounds are:
Butane-1,4-diisocyanate, 2376
† Butyl isocyanate, 1931
4-Chlorophenyl isocyanate, 2648
1,6-Diisocyanatohexane, 3008
Diisocyanatomethane, 1079
2,4-Diisocyanatotoluene, 3117
† Methyl isocyanate, 0761
1-Naphthyl isocyanate, 3390
2-Phenylethyl isocyanate, 3139
Phenyl isocyanate, 2685
∗ Trifluoromethyliodine(III) isocyanate, 1045
See Potassium cyanate

ORGANIC PEROXIDES **C−OO**

1. Noller, D. C. *et al., Anal. Chem.*, 1963, **35**, 887–893
2. Castrantas, 1970
3. Varjarvandi, J. *et al., J. Chem. Educ.*, 1971, **48**, A451
4. *Code of Practice for Storing and Handling of Organic Peroxides*, P15.1, Luton, Interox Chemicals, 1975
   Storage and Handling of Organic Peroxides, Guidance Note CS 21, HMSO, London.
5. Jackson, H. L., *J. Chem. Educ.*, 1970, **47**, A175
6. Castrantas, 1965
7. Davies, 1961
8. Swern, 1970, Vol. 1, 1–104
9. Houben-Weyl, 1952, Vol. 8.3, 1
10. Swern, 1972, Vol. 3, 341–364
11. Stevens, H. C., US Pat. 2 415 971, 1947
12. Cookson, P. G. *et al., J. Chem. Soc., Chem. Comm.*, 1976, 1022–1023
13. Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 32
14. Kotani, M. *et al., Chem. Abs.*, 1980, **92**, 87594
15. Marisaki, S., *Chem. Abs.*, 1983, **98**, 34100
16. Matsunaga, T. *et al., Chem. Abs.*, 1984, **101**, 113378
17. Halle, R., *Chem. Eng. News*, 1984, **62**(47), 4
18. Tamura, M. *et al., J. Haz. Mat.*, 1987, **17**(1), 89–98
19. Mackenzie J., *Plant/Oper. Progr.*, 1991, **10**(3), 165
20. Anon., *Jahresber.*, 1987, 65

Of the general guides to the safe handling and use of peroxides, the third and second include details of hazard evaluation tests, and the first has a comprehensive bibliography [1,2,3]. Storage aspects are rather specific [2,4]. Procedures for the safe handling of peroxidisable compounds have also been described [5]. Tabulated data on fire and explosion hazards of classes of organic peroxides with an extensive bibliography were published [6]. Theoretical aspects have been considered [6,7,8], the practical hazards involved in synthesis of organic peroxides have been

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detailed [9], and a further review on the evaluation and management of peroxide hazards appeared [10]. The use of iodine to stabilise liquid organic peroxides against explosive or incendiary decomposition has been claimed [11]. A new safe general method for rapid preparation of n-, *sec*- or *tert*-alkyl hydroperoxides has been described [12]. Leakage of an organic peroxide catalyst solution into pipe lagging exposed to direct solar radiation led to a fire [13].

Pyrolysis GLC has been used to develop a safe method for the qualitative determination of thermally unstable organic peroxides like benzyl peroxide. The mechanism of decomposition reactions and the temperature limits for safe handling of peroxides can also be determined by this technique [14]. In a study of adiabatic thermal decomposition, 2 g samples of di-*tert*-butyl and dibenzoyl peroxides, *tert*-butyl peroxybenzoate and peroxy-2-ethylhexanoate attained maximum self-heating rates and final pressures of 150–440°C/min and 4.5–9.5 kbar, respectively [15]. Group contributions to heat of formation (l) were derived from suitable reference compounds and used to estimate ΔH_f° for peroxides by additivity methods. The agreement between calculated and observed values were good enough to estimate hazard properties for energetic materials such as peroxides [16]. A general measure of the degree of hazard associated with an organic peroxide may be gained from the content of 'active oxygen' (AO, or wt% of peroxidic oxygen) in the molecule. Thus 2,2-bis(hydroperoxy)propane (highly explosive) with 30.2% AO has an extremely high value compared to the 1–17% commonly encountered in commercial organic peroxides, e.g. MEK peroxide, which is supplied and handled safely as a solution diluted to a maximum AO content of 9% [17].

Work on the deflagration hazards of organic peroxides has been done using a revised Time–Pressure test, to determine the characteristics of ignition sensitivity and violence of deflagration. Some correlation is evident between these characteristics and the AO content within each structurally based peroxide type. Also, for the same AO content, the nature of the characteristics appears to decrease in the order diacyl peroxides, peroxyesters, dialkyl peroxides, alkylhydroperoxides [18].

Warning is given that sodium sulfite may not remove all peroxidic compounds if peroxyacids are present, with which it can form undetectable, but unstable, complex peroxides [19]. Peroxide test strips may not be sufficiently reliable as the sole means of testing for presence of peroxides in a wide range of peroxidisable liquids. It was recommended that an additional test (potassium iodide–acetic acid) should be used unless it is certain that the test strips will give a positive result with a particular peroxide-containing liquid [20].

Except for the peroxides individually listed below, all index entries have been assigned to the structurally based groups:

ALKYL HYDROPEROXIDES, *tert*-BUTYL PEROXOPHOSPHATE DERIVATIVES
CYCLIC PEROXIDES, DIACYL PEROXIDES
DIALKYL PEROXIDES, DIOXETANES
KETONE PEROXIDES, 1-OXYPEROXY COMPOUNDS
OZONIDES, PEROXYACIDS
PEROXYCARBONATE ESTERS, PEROXYESTERS
α-PHENYLAZO HYDROPEROXIDES, POLYPEROXIDES

Individually indexed compounds are:

- Chloroperoxytrifluoromethane, 0319
- Perfluoro-*tert*-butyl peroxyhypofluorite, 1373
- Peroxypropionyl perchlorate, 1167
- 3,3,5-Triphenyl-4,4-dimethyl-5-hydroperoxy-4,5-dihydro(3H)pyrazole, 3841

See also COMMERCIAL ORGANIC PEROXIDES

ORGANIC POWDER HANDLING

Electrostatic hazards in powder handling, Gior, M., Letchworth, Research Study Press, 1988 (also from Wiley)

The role of electrostatic generation as an important ignition source in industrial powder handling operations is discussed in this book.

See DUST EXPLOSION INCIDENTS, ELECTROSTATIC HAZARDS, IGNITION SOURCES

ORGANOLITHIUM REAGENTS XArLi

1. Bretherick, L., *Chem. & Ind.*, 1971, 1017
2. Gilman, H., private comm., 1971
3. 'Benzotrifluorides Catalog 6/15', West Chester (Pa.), Marshallton Res. Labs., 1971
4. Coates, 1960, 19
5. *MCA Case History No. 1834*
6. Anderson, R., *Chem. & Ind.*, 1984, 205208
7. Wakefield, B. J., *Organolithium Methods*, London, Academic, 1988

DropBooks

Several halo-aryllithium compounds are explosive in the solid state in absence or near-absence of solvents or diluents, and operations should be designed to avoid their separation from solution. Such compounds include *m*- and *p*-bromo-, *m*-chloro-, *p*-fluoro-, *m*- and *p*-trifluoromethyl-phenyllithiums [1] and 3,4-dichloro-2,5-dilithiothiphene [2], but *m*-bromo- and *o*-trifluoromethyl-phenyllithium appear to be explosive in presence of solvent also [1,3]. The *m*- and *p*-dilithiobenzenes are also explosively unstable under certain conditions. Most organolithium compounds are pyrophoric when pure (especially those of high lithium content) and are usually handled in solution and under inert atmosphere [4]. A completed preparation of *o*-trifluoromethylphenyllithium refluxing in ether under nitrogen suddenly exploded violently [5]. Equipment and procedures necessary for the safe use of organolithium reagents on the industrial scale have been detailed [6]. Aspects of practical significance (solvents, inert atmospheres, equipment, and handling procedures) related to the safe use of organolithium reagents are included in the volume [7].

Examples of these compounds may be found in the group:

FLUORINATED ORGANOLITHIUM COMPOUND

and the individual entries:

3-Bromophenyllithium, 2129
4-Bromophenyllithium, 2130
3-Chlorophenyllithium, 2138

4-Chlorophenyllithium, 2139
3,4-Dichloro-2,5-dilithiothiophene, 1357
1,3-Dilithiobenzene, 2178
1,4-Dilithiobenzene, 2179
4-Fluorophenyllithium, 2166
2-,3- or 4-Trifluoromethylphenyllithium, 2657

See other HALO-ARYLMETALS

ORGANOMETALLIC NITRATES

These compounds, although not as dangerous as the related perchlorates, have a reducing organic moiety in intimate association with an oxidant nitrate, combined with a metal which may well be an oxidation catalyst. They feature increasingly as explosive compounds in reports too numerous to feature all as individual entries in a handbook. These comments apply equally to the complexed species loosely described as organometallic although lacking a carbon–metal bond. Individual compounds include:

η^6-Benzeneruthenium(II) dinitrate, 2320
Dimethyltin dinitrate, 0914
2-Hydroxyethylmercury(II) nitrate, 0857
2-Methyl-1-nitratodimercurio-2-nitratomercuriopropane, 1592

See METAL NITRATES, AMMINEMETAL OXOSALTS

ORGANOMETALLIC PERCHLORATES

The comments on organometallic nitrates, above, apply with redoubled force here. Although becoming fewer as chemists learn caution, reports of explosion are even more numerous than for the nitrates, and the explosions are more powerful. Again far from all reported have been given entries. Individual compounds are :

See PERCHLORATES, METAL PERCHLORATES, AMMINEMETAL OXOSALTS

ORGANOMETALLIC PEROXIDES **RM−OO, RE−OO**

1. Castrantas, 1965, 18
2. Swern, 1970, Vol. 1, 13
3. Sosnovsky, G. *et al., Chem. Rev.*, 1966, **66**, 529
4. Colletti, S. L. *et al., J. Organomet. Chem.*, 1993, **455**(1–2), 99

Available information suggests that both hydroperoxides and peroxides in this extensive group of compounds are in many cases stable to heat at temperatures rather below 100°C, but may decompose explosively at higher temperatures. There are, however, exceptions [1]–[3]. Organoniobium peroxides may be explosive when exposed to air [4]. Individually indexed compounds are:

∗ Bis(methylcyclopentadienyl)peroxoniobium chloride, 3522
Bis(triethyltin) peroxide, 3581
Dicyclopentadienylperoxyniobium chloride, 3271
Diethylhydroxytin hydroperoxide, 1763
Di(hydroperoxy)trimethylantimony(V), 1333

Methylbis(η^2-peroxo)rhenium oxide hydrate, 0497
Triethyltin hydroperoxide, 2583
Trimethylsilyl hydroperoxide, 1330
Triphenyltin hydroperoxide, 3758

See also ALKYL TRIALKYLLEAD PEROXIDES

ORGANOMETALLICS C−M

High Energy Processes in Organometallic Chemistry, Suslick, K. S. (ed.), ACS Symp. Ser. No 333, Washington, ACS, 1987

Several of the chapters in this 336 page book are concerned with the preparation, properties and use of very highly reactive materials in organometallic chemistry.

This class of rather miscellaneous organometallic compounds, all with carbon−metal bonding, contains the separately treated groups:

ALKYLMETAL HALIDES, ALKYLMETALS
ARYLMETALS, 1-ARYL-1-VINYLLITHIUM DERIVATIVES
GRIGNARD REAGENTS, HALO-ARYLMETALS
ORGANOLITHIUM REAGENTS

and the individually indexed compounds:

∗ Benzylsodium, 2787
∗ Bis(η-benzene)chromium(0), 3511
Bis(benzene)chromium dichromate, 3851
∗ Bis(η-benzene)iron(0), 3512
Bis(benzeneiron)−fulvalenediyl complex, 3834
∗ Bis(η-benzene)molybdenum(0), 3514
Bis(cyclooctatetraene)uranium(0), 3708
Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium, 3830
Bis(cyclopentadienyldinitrosylchromium), 3275
Bis(cyclopentadienyl)hexafluoro-2-butynechromium, 3636
Bis(cyclopentadienyl)lead, 3294
Bis(cyclopentadienyl)magnesium, 3277
Bis(cyclopentadienyl)manganese, 3278
Bis(cyclopentadienyl)niobium tetrahydroborate, 3324
∗ Bis(cyclopentadienyl)pentafluorophenylzirconium hydroxide, 3703
∗ Bis(cyclopentadienyl)phenylvanadium, 3705
Bis(cyclopentadienyl)titanium, 3295
Bis(cyclopentadienyl)titanium selenate, 3293
Bis(cyclopentadienyl)zirconium, 3296
Bis(dicarbonylcyclopentadienyliron)−bis(tetrahydrofuran)magnesium, 3835
∗ Bis[dicarbonyl(cyclopentadienyl)tributylphosphinemolybdenum]−tetrakis(tetrahydrofuran)magnesium, 3913
Bis(μ_3-methylidyne)*triangulo* tris(pentamethylcyclopentadienylrhodium), 3879
Bis(pentafluorophenyl)ytterbium, 3423

BioOpenBooks

∗ Bis(2,4-pentanedionato)chromium, 3326
Chloro(η^8 1,3,5,7-cyclooctatetraene)(tetrahydrofuran)lutetium, 3536
∗ (η^8 1,3,5,7-Cyclooctatetraene)[2-(dimethylaminomethyl)phenyl-*C*,*N*](tetrahydrofuran)lutetium, 3826
μ-Cyclopentadienyl(methyl)-bis-(*N*-methyl-*N*-nitrosohydroxylamino) titanium, 3028
Cyclopentadienylsodium, 1855
μ-Cyclopentadienyltrimethyltitanium, 3038
Diaquabis(cyclopentadienyl)titanium dichromate, 3327
1,3-Di[bis(cyclopentadienyl)iron]-2-propen-1-one, 3840
∗ Dicarbonyl-π-cycloheptatrienyltungsten azide, 3123
cis-Dicarbonyl(cyclopentadienyl)cyclooctenemanganese, 3681
∗ (2,2-Dichloro-1-fluorovinyl)ferrocene, 3470
Dicumenechromium(0), 3767
Dicyclopentadienylchromium, 3273
4,4-Diferrocenylpentanoyl chloride, 3859
Dilithium μ-cyclooctatetraene, 2948
Dimethylaminomethylferrocene, 3613
2-(Dimethylaminomethyl)fluoroferrocene, 3612
Dipotassium μ-cyclooctatetraene, 2947
Ferrocene, 3276
∗ Ferrocene-1,1′-dicarboxylic acid, 3479
∗ 1-Ferrocenyl-2-methylpropyl azide, 3661
∗ Methylaluminiumbis(pentamethylcyclopentadienyltrimethyliridium), 3866
Nickelocene, 3287
Oxybis[bis(cyclopentadienyl)titanium], 3803
Pentamethylcyclopentadienyl-bis(thiolatothiatriazyl)rhodium, 3534
Poly(cyclopentadienyltitanium dichloride), 1843
∗ Tricyclopentadienyluranium tetrahydroaluminate, 3688
N,*N*,4-Trilithioaniline, 2180
Triphenylmethylpotassium, 3781
Tris(cyclopentadienyl)cerium, 3683
Tris(cyclopentadienyl)plutonium, 3684
Tris(cyclopentadienyl)uranium, 3685
∗ Tris(2,4-pentanedionato)molybdenum(III), 3690

ORGANOSILYL PERCHLORATES **R_3SiClO_4**

Wannagat, U. *et al., Z. Anorg. Chem.*, 1950, **302**, 185–198
Several trialkyl- or triaryl-silyl perchlorates explode on heating, including:
Triethylsilyl perchlorate, 2562
Tri-4-methylphenylsilyl perchlorate, 3823
Trimethylsilyl perchlorate, 1302

Triphenylsilyl perchlorate, 3750
Tripropylsilyl perchlorate, 3218
See related NON-METAL PERCHLORATES

ORIGINS OF UNWANTED CHEMICAL REACTIONS

Rasmussen, B., *Unwanted Chemical Reactions in Chem. Processing Ind.*, Rept. M-2631, Roskilde (DK), Riso National Lab., 1987

A total of 190 published case histories of chemical processing accidents, selected from the MCA series, *Loss Prevention Bulletin, Loss Prevention* and elsewhere have been analysed to determine the underlying reasons for the unwanted chemical reactions. The most common reasons were:- incorrect storage or handling of materials, (24%); contamination or catalytic impurities, (20%); use of wrong chemicals, (19%); incorrect charging or processing conditions, (19%); insufficient agitation, (13%). Accidents in batch reactors were much more frequent than in continuous reactors.

In 55% of the cases, the accidents could have been foreseen by use of risk analysis, and in 35% of the cases by thermal stability testing. Different methods of stability testing were evaluated comparatively during the investigation of a runaway exothermic reaction which occurred during the preparation of a component mixture for a sealing composition in a 1200 l reactor: only DSC was effective in identifying the cause of the hazard.

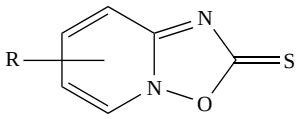
A series of checklists is proposed to avoid such incidents in chemical processing operations, and an incompatibility chart for groups of reactive chemicals is given.

The methods used for the analysis of the case histories are detailed in a separate Appendix A, (Riso-278).

DropBooks

See Lead(IV) oxide: Carbon black, Chlorinated paraffin, Manganese(IV) oxide
See CATALYTIC IMPURITY INCIDENTS, AGITATION INCIDENTS, RUNAWAY REACTIONS
See also ACCELERATING RATE CALORIMETRY, REACTION SAFETY CALORIMETRY

2*H*-1,2,4-OXADIAZOLO[2,3-a]PYRIDINE-2-THIONES



Rousseau, D. *et al.*, *Can. J. Chem.*, 1977, **55**, 3736–3739

The title compounds (R = H, 5-, 6-, 7-, or 8-methyl, or 5,7-dimethyl) explode at 121–137°C.

See other N–O COMPOUNDS

OXIDANTS

1. *Inorganic High Energy Oxidisers: Synthesis, Structure and Properties*, Lawless, E. W. and Smith, I. C., London, Arnold, 1968
2. *Hazard Classification of Oxidising Materials and Flammable Solids*, King P. V. *et al.*, Rept. PB-220084, Washington, US Dept. Transport, 1972
3. *NFPA 43A*, 1980; *NFPA 43B*, 1986; *NFPA 43C*, 1986, Quincy (Ma), National Fire Protection Association

Developments in inorganic fluorine oxidants, largely for rocketry, are covered [1]. A method of rating the potency of oxidants involves heating a carefully prepared and blended mixture of the solid oxidant with size-graded dried sawdust at 38.5°C/10 min to assess gross self-heating and ignition capability. Then a rectangular bed 2.5 cm deep x 5 x 17.5 cm is ignited at one end and the time taken for the combustion front to traverse 12.5 cm is taken as an inverse measure of oxidising power [2]. Three recent US fire codes cover the storage requirements for liquid or solid oxidants; for formulated organic peroxides; and for gaseous oxidants, respectively [3].

Members of this class of materials have been involved in the majority of the two-component reactive systems included in this Handbook, and the whole class is extremely large. Most oxidants have been treated collectively in the structurally based entries:

ACETYLENIC PEROXIDES, ACYL HYPOHALITES
ALKYL HYDROPEROXIDES, ALKYL TRIALKYLLEAD PEROXIDES
AMINIUM IODATES AND PERIODATES, AMMINECHROMIUM PEROXOCOMPLEXES
BIS(FLUOROOXY)PERHALOALKANES, BLEACHING POWDER, CHLORITE SALTS
COMMERCIAL ORGANIC PEROXIDES, CRYSTALLINE HYDROGEN PEROXIDATES
CYCLIC PEROXIDES, DIACYL PEROXIDES
DIALKYL PEROXIDES, *I,I*-DI(BENZOYLPEROXY)ARYLIODINES
DIFLUOROAMINO COMPOUNDS, DIFLUOROAMINOPOLYNITROAROMATIC COMPOUNDS
DIFLUOROPERCHLORYL SALTS, DIOXETANES
DIOXYGENYL POLYFLUOROSALTS, FLUORINATED PEROXIDES AND SALTS
FLUORODINITRO COMPOUNDS, *N*-HALOGEN COMPOUNDS
HALOGEN OXIDES, HALOGENS
N-HALOIMIDES, HEXAFLUOROCHLORONIUM SALTS
HYDROXOOXODIPEROXOCHROMATE SALTS, HYPOHALITES
INORGANIC PEROXIDES, INTERHALOGENS
KETONE PEROXIDES, LIQUID AIR
METAL CHLORATES, METAL HALOGENATES
METAL HYPOCHLORITES, METAL NITRATES
METAL NITRITES, METAL OXOHALOGENATES
METAL OXOMETALLATES, METAL OXONON-METALLATES
METAL OXIDES, METAL PERCHLORATES
METAL PEROXIDES, METAL PEROXOMOLYBDATES

METAL POLYHALOHALOGENATES, MOLTEN SALT BATHS
NITROALKANES, NON-METAL PERCHLORATES
OXIDES OF NITROGEN
OXOHALOGEN ACIDS, OXYGEN ENRICHMENT
1-OXYPEROXY COMPOUNDS, OZONIDES
PERCHLORYL COMPOUNDS, PEROXOACIDS
PEROXOACID SALTS, PEROXYACIDS
PEROXYCARBONATE ESTERS, PEROXYESTERS
POLYNITROALKYL COMPOUNDS, POLYPEROXIDES
QUATERNARY OXIDANTS, TRINITROETHYL ORTHOESTERS
XENON COMPOUNDS

Other individually indexed compounds are:

Acetyl hypofluorite, 0751
∗ Ammonium hexanitrocerate, 3964
∗ Ammonium nitrate, 4522
Ammonium permanganate, 4518
Ammonium peroxodisulfate, 4576
Antimony pentachloride, 4184
Barium chlorite, 0204
Barium peroxide, 0216
∗ Bismuthic acid, 0228
Bromine, 0261
4-*tert*-Butyliodylbenzene, 3319
Caesium fluoroxysulfate, 4256
Calcium chromate, 3926
∗ Calcium hypochlorite, 3924
Calcium nitrate, 3935
Calcium permanganate, 3934
Calcium peroxide, 3938
Calcium peroxodisulfate, 3940
Calcium triperoxochromate, 3945
Chlorine, 4047
Chlorine dioxide, 4042
Chlorosulfuric acid, 3997
Chloryl perchlorate, 4104
Chromic acid, 4229
Chromium pentafluoride, 4226
Chromium trioxide, 4242
Chromyl acetate, 1494
∗ Chromyl chloride, 4054
∗ Chromyl fluorosulfate, 4225
∗ Chromyl perchlorate, 4055
Cobalt(II) nitrate, 4215
Di-*tert*-butyl chromate, 3066
Dichlorine oxide, 4095

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Dilead(II)lead(IV) oxide, 4861
Dinitrogen oxide, 4744
Dinitrogen pentaoxide, 4748
Dinitrogen tetraoxide, 4747
Dinitrogen trioxide, 4746
Dioxonium hexamanganato(VII)manganate, 4553
Dioxygen difluoride, 4320
Dioxygenyl tetrafluoroborate, 0132
Dipyridinium dichromate, 3304
Fluorine, 4310
Fluorine fluorosulfate, 4324
Fluoroselenic acid, 4295
Graphite hexafluorogermanate, 3422
1,1,1,3,5,5,5-Heptanitropentane, 1854
Hydrogen peroxide, 4477
Iodic acid, 4424
Iodine, 4625
Iodine dioxide trifluoride, 4334
Iodine(V) oxide, 4627
Iodine(VII) oxide, 4628
Iridium hexafluoride, 4362
Lead chromate, 4243
Lead(II) nitrate, 4749
Lead(II) oxide, 4824
Lead(IV) oxide, 4834
Lithium chlorite, 4020
Magnesium nitrite, 4692
Magnesium nitrate, 4693
Magnesium permanganate, 4691
∗ Manganese fluoride trioxide, 4301
Manganese(IV) oxide, 4705
Manganese(VII) oxide, 4709
Manganese tetrafluoride, 4343
Mercury(II) bromate, 0270
Mercury(II) nitrate, 4603
Mercury(II) oxide, 4605
Monofluoroxonium hexafluoroarsenate, 0097
Neptunium hexafluoride, 4366
Nickel(II) nitrate, 4743
Nitric acid, 4436
Nitrogen dioxide, 4725
Nitrogen oxide, 4724
Nitrosyl chloride, 4023
Nitrosyl fluoride, 4302
Nitrosyl perchlorate, 4027
Nitrosylsulfuric acid, 4438

Nitrosyl tetrafluorochlorate, 3985
Nitrous acid, 4435
Nitryl chloride, 4025
Nitryl fluoride, 4303
Nitryl hypochlorite, 4026
Nitryl hypofluorite, 4304
Nitryl perchlorate, 4029
Osmium hexafluoride, 4370
Osmium(VIII) oxide, 4858
Oxygen (Gas), 4831
Oxygen (Liquid), 4832
Oxygen difluoride, 4317
Ozone, 4846
Palladium(II) oxide, 4825
Palladium(IV) oxide, 4835
Perchloric acid, 3998
Periodic acid, 4425
Permanganic acid, 4434
Peroxodisulfuric acid, 4482
Peroxodisulfuryl difluoride, 4328
Peroxomonosulfuric acid, 4481
Peroxytrifluoroacetic acid, 0666
Platinum hexafluoride, 4371
Platinum(IV) oxide, 4836
Plutonium hexafluoride, 4372
Potassium bromate, 0255
Potassium chlorate, 4017
Potassium dichromate, 4248
Potassium iodate, 4619
Potassium nitrate, 4650
Potassium nitrite, 4649
Potassium perchlorate, 4018
Potassium periodate, 4620
Potassium permanganate, 4647
Rhenium hexafluoride, 4373
Rubidium fluoroxysulfate, 4309
Ruthenium(VIII) oxide, 4862
Selenium dioxide, 4838
* Selenium dioxide, 4838
Silver permanganate, 0021
Sodium chlorate, 4039
Sodium chlorite, 4038
Sodium dichromate, 4250
Sodium iodate, 4624
Sodium nitrate, 4721
Sodium nitrite, 4720

DropBooks

Sodium perchlorate, 4040
Sodium permanganate, 4703
Sodium peroxide, 4803
Sodium peroxodisulfate, 4809
† Sulfur, 4897
Sulfuric acid, 4479
Sulfur trioxide, 4849
Tetrafluoroammonium hexafluoromanganate, 4384
Tetrafluoroammonium hexafluoronickelate, 4385
Tetrafluoroammonium hexafluoroxenate
Tetranitromethane, 0546
Titanium tetraperchlorate, 4170
1,1,1-Triacetoxy-1,2-benziodoxol-3-one, 3610
Trifluoromethyl hypofluorite, 0353
Trimethylsilyl chlorochromate, 1301
'Trioxygen difluoride', 4323
Uranium hexafluoride, 4375
Vanadium(V) oxide, 4866
∗ Vanadium trinitrate oxide, 4763
Vanadyl perchlorate, 4152
Xenon hexafluoride, 4377
Xenon(II) pentafluoroorthoselenate, 4382
Xenon(II) pentafluoroorthotellurate, 4383
Xenon tetrafluoride, 4353
Xenon tetrafluoride oxide, 4346
Xenon tetraoxide, 4863
Xenon trioxide, 4857
Zinc permanganate, 4710

OXIDANTS AS HERBICIDES

Cook, W. H., *Can. J. Res.*, 1933, **8**, 509

The effect of humidity on combustibility of various mixtures of organic matter and sodium chlorate was studied. Addition of a proportion of hygroscopic material (calcium or magnesium chlorides) effectively reduces the hazard. Similar effects were found for sodium dichromate and barium chlorate.

See Sodium chlorate: Organic matter

OXIDATION INCIDENTS

Since the vast majority of the hazardous occurrences described in this volume involve oxidation reactions, it is not feasible to provide a comprehensive listing of the individual incidents. However, it may be noted that nitric acid and hydrogen peroxide are the two common oxidants most frequently involved in accidents.

See MICROWAVE OVEN HEATING, OXIDANTS, OXIDATION PROCESSES, SAMPLE DISSOLUTION

See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

OXIDATION PROCESSES

Kletz, T. A., *Plant/Oper. Progr.*, 1988, **7**, 226–230

Fire and explosion hazards of processes involving the oxidation of hydrocarbons are reviewed, including oxidation of cyclohexane to cyclohexanone/cyclohexanol, ethylene to ethylene oxide, of cumene to its hydroperoxide, and of *p*-xylene to terephthalic acid.

N-OXIDES **N → O**

Baumgarten, H. E. *et al., J. Amer. Chem. Soc.*, 1957, **79**, 3145

A procedure for preparing *N*-oxides is described which avoids formation of peroxyacetic acid. After prolonged treatment of the amine at 35–40°C with excess 30% hydrogen peroxide, excess of the latter is catalytically decomposed with platinum oxide.

Individually indexed compounds are:

2-Bromo-4-methylpyridine *N*-oxide, 2297
3-Bromopyridine *N*-oxide, 1828
∗ Decafluoro-2,5-diazahexane 2,5-dioxyl, 1372
2,3-Diazabicyclo[2.2.2]octa-2,5-diene *N*-oxide, 2374
5,6-Diphenyl-1,2,4-triazine-3-diazonium tetrafluoroborate 2-oxide, 3677
∗ Disodium 5,5′-azoxytetrazolide, 1019
Fulminic acid, 0381
4(1-Hydroxyethyl)pyridine *N*-oxide, 2820
1-Hydroxyimidazole *N*-oxide, 1134
N-Methylmorpholine oxide, 1997
3-Methyl-4-nitropyridine *N*-oxide, 2317
N-Methylpiperidine–$N\frac{1}{2}$-oxide
2-(*N*-Nitroamino)pyridine *N*-oxide, 1851
4-(*N*-Nitroamino)pyridine *N*-oxide, 1852
2,2′-bipyridyl 1-oxide, 3258
4-Nitropyridine *N*-oxide, 1833
2,2′-Oxybis(iminomethylfuran) mono-*N*-oxide, 3260
Pyridine *N*-oxide, 1849
Tribromamine oxide, 0291
Trimethylamine oxide, 1313

See FURAZAN *N*-OXIDES

ProBooks

OXIDES OF NITROGEN **NO_n**

The oxides of nitrogen collectively are oxidants with power increasing with oxygen content. Dinitrogen oxide will often support violent combustion, since its oxygen content (36.5%) approaches double that of atmospheric air. Nitrogen oxide and dinitrogen oxide are both endothermic and capable of detonation in the liquid state. Individually indexed oxides are:

Dinitrogen oxide
Dinitrogen pentaoxide
Dinitrogen tetraoxide
Dinitrogen trioxide
Nitrogen dioxide
Nitrogen oxide

Glyptal resin

Anon., *ABCM Quart Safety Summ.*, 1937, **8**, 31

A new wooden fume cupboard was varnished with glyptal (glyceryl phthalate) resin. After a few weeks' use with 'nitrous fumes', the resin spontaneously and violently ignited. This was attributed to formation and decomposition of glyceryl trinitrate or similar compounds.

Oxides of nitrogen are thought to have been involved in several violent incidents.

See Hydrogen (Gas), : Liquid nitrogen, 4453
Nitrogen oxide, : Dienes, Oxygen, 4724
Nitrogen dioxide, : Alkenes, 4725
Dinitrogen tetraoxide, : Unsaturated hydrocarbons, 4747

In this latter context, however, according to Henstock, W. H., *Plant/Oper. Progr.*, 1986, **5**, 232–237, no explosive products from hydrocarbon/oxides of nitrogen contact were found in a cryogenic hydrogen recovery unit processing petroleum refinery gases and cracked gases, and no such hazardous reactions seemed likely.

See other OXIDANTS

OXIME CARBAMATES **C=NOCO.NHR**

Pinnegar, M. A. *et al.*, UK Pat. 2 000 031, 1979

Oxime carbamates may explode on heating, after an induction period of very variable length, dependent upon temperature and impurities present.

See other INDUCTION PERIOD INCIDENTS, N–O COMPOUNDS

See also OXIMES

OXIMES **RC=NOH**

1. Horner, L. in *Autoxidation and Antioxidants*, Lundberg, W. O. (Ed.), Vol. 1, 184–186, 197–202, New York, Interscience, 1961
2. Tyler, L. J., *Chem. Eng. News*, 1974, **52**(35), 3
3. Cardillo, P. *et al., J. Loss Prev.*, 1993, **6**(2), 69

Several explosions or violent decompositions during distillation of aldoximes may be attributable to presence of peroxides arising from autoxidation. The peroxides may form on the −C=NOH system (both aldehydes and hydroxylamines peroxidise [1]) or perhaps arise from unreacted aldehyde. Attention has been drawn to an explosion hazard inherent to ketoximes and many of their derivatives (and not limited to them). The hazard is attributed to inadvertent occurence of acidic conditions leading to highly exothermic Beckmann rearrangement reactions accompanied by potentially catastrophic gas evolution. Presence of acidic salts (iron(III)

chloride, or the ketoxime hydrochloride) markedly lowers decomposition temperatures [2].

A nickel catalysed aldoxime rearrangement, to an amide, went out of control after changing the solvent employed. This was found to be due to a slow start and consequent accumulation of unreacted substrate. Changing to a higher operating temperature restored control to the process [3].

Individually indexed compounds are:

† Acetaldehyde oxime, 0865
Acetone oxime, 1258
Azoformaldoxime, 0815
Benzaldehyde oxime, 2760
Bromoacetone oxime, 1201
Butane-2,3-dione dioxime, 1595
2,3-Butanedione monoxime, 1570
2-Butanone oxime, 1654
∗ 2-Butanone oxime hydrochloride, 1678
Butyraldehyde oxime, 1655
'10-Carbon oxime', 3362
Chloroacetaldehyde oxime, 0787
∗ 2-Chloro-*N*-hydroxyacetamidine, 0849
1,2,3-Cyclohexanetrione trioxime, 2400
1,3,5-Cyclohexanetrione trioxime, 2401
Cyclohexanone oxime, 2452
Cyclopentanone oxime, 1932
2,3-Epoxypropionaldehyde oxime, 1182
2-Ethylacryladehyde oxime, 1933
Ethyl 2-formylpropionate oxime, 2454
Furan-2-amidoxime, 1872
∗ Hydroxycopper(II) glyoximate, 0799
1-Hydroxyimidazole-2-carboxaldoxime 3-oxide, 1477
2-Isopropylacrylaldehyde oxime, 2453
∗ *N*-Methoxy-*N*-methylbenzylidenimmonium methylsulfate, 3334
2-Methyl-2-[4-(2-methylpropyl)phenyl]oximinoethane, 3614
2-Nitroacetaldehyde oxime, 0809
1-Nitro-1-oximinoethane, 0810
∗ Nitrooximinomethane, 0409
3-(2-Nitrophenyl)-2-hydroxyiminopropanoic acid, 3131
2-Nitrosophenol (1,2-Benzoquinone monoxime), 2263
∗ 4-Nitrosophenol (1,4-Benzoquinone monoxime), 2264
4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2357
∗ Potassium cyclohexanehexone 1,3,5-trioximate, 2625
∗ Potassium 1-nitroethane-1-oximate, 0756
∗ Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1409
Sodium 2-allyloxy-6-nitrophenylpyruvate oxime, 3505
∗ Sodium 4-chloroacetophenone oximate, 2927

DropBooks

∗ Sodium 3-methylisoxazolin-4,5-dione-4-oximate, 1419
∗ Sodium 3-phenylisoxazolin-4,5-dione-4-oximate, 3114
∗ Sodium tris(*O*,*O*′-1-oximatonaphthalene-1,2-dione)ferrate, 3871
Trichloroacetaldehyde oxime, 0698
∗ Trinitrosophloroglucinol, 2117
See KETOXIMINOSILANES

OXOHALOGEN ACIDS $HOXO_n$

1. Bretherick, L., Comments, 1970
2. Alazard, J-P.*et al.*, *Actual. Chim.*, 1995, (1), 49

The oxidising power of the group of oxohalogen acids increases directly with oxygen content, though the high stability of the perchlorate ion at ambient temperature must be taken into account. The corresponding 'anhydrides' (halogen oxides) are also powerful oxidants, several being explosively unstable [1]. A review has been published on the instability of, and consequent safety considerations for, oxygen derivatives of chlorine; oxides, acids and salts thereof, used in organic synthesis [2].

Individual compounds are:
Bromic acid, 0248
Chloric acid, 3996
Hypochlorous acid, 3995
Iodic acid, 4424
Orthoperiodic acid, 4542
Perchloric acid, 3998
Periodic acid, 4425
See also HALOGEN OXIDES

OXOSALTS OF NITROGENOUS BASES $N^+ EO_n^-$

1. Fogel'zang, A. G. *et al.*, *Chem. Abs.*, 1971, **75**, 142412
2. Mikhailova, T. A. *et al.*, *Chem. Abs.*, 1976, **85**, 201766

Burning rates of ammonium salts were investigated at various constant pressures. Ammonium permanganate burns faster than ammonium bromate, chlorate, dichromate, iodate, nitrite, perchlorate, periodate or triperchromate [1]. When submitting explosive nitrogenous bases or their salts to elemental nitrogen determination, it is advantageous to pre-treat the samples with phosphoric acid which allows the more stable pyro- and meta-phosphates (formed at 260° and 300°C, respectively) to be fully oxidised without explosion in the Dumas nitrogen procedure [2].

Many of the salts of nitrogenous bases (particularly of high nitrogen content) with oxoacids are unstable or explosive. There are separate group entries for:

AMINIUM IODATES AND PERIODATES, AMINIUM PERCHLORATES
DIAZONIUM PERCHLORATES, DICHROMATE SALTS OF NITROGENOUS BASES
1-(1,3-DISELENONYLIDENE)PIPERIDINIUM PERCHLORATES
HYDRAZINIUM SALTS, HYDROXYLAMINIUM SALTS

Individually indexed compounds are:

∗ Ammonium amidoselenate, 4557
Ammonium amidosulfate, 4556
Ammonium bromate, 0252
Ammonium chlorate, 4003
∗ Ammonium fluorochromate, 4224
∗ Ammonium nitrate, 4522
Ammonium permanganate, 4518
Ammonium tetrachromate(2−), 4253
Ammonium tetranitroplatinate(II), 4578
Ammonium trichromate(2−), 4252
Anilinium nitrate, 2379
2,2′-Azobis(2-amidiniopropane) peroxodisulfate, 3091
3-Azoniabicyclo[3.2.2]nonane nitrate, 3048
Chloroformamidinium nitrate, 0467
4-Chloro-1-methylimidazolium nitrate, 1453
1-(4-Chlorophenyl)biguanidinium hydrogen dichromate, 3005
Diaminoguanidinium nitrate, 0514
1,2-Diammonioethane nitrate, 0966
∗ 2-Diethylammonioethyl nitrate nitrate, 2571
Guanidinium nitrate, 0509
Hydrazinium chlorate, 4010
Hydrazinium dinitrate, 4561
Hydrazinium hydrogen selenate, 4558
Hydrazinium nitrate, 4549
Hydroxylaminium nitrate, 4524
2-Methoxyanilinium nitrate, 2829
Methylammonium chlorite, 0500
Methylammonium nitrate, 0506
Methylammonium nitrite, 0505
Methylhydrazinium nitrate, 0511
1-Methyl-3-nitroguanidinium nitrate, 0947
1-Phenylbiguanidinium hydrogen dichromate, 3019
Pyridinium nitrate, 1873
1,3,6,8-Tetraazoniatricyclo[6.2.1.1^{3,6}]dodecane tetranitrate, 3092
Tetraethylammonium periodate, 3090
Tetrafluoroammonium perbromate, 0242
∗ Tetrakis(hydroxymethyl)phosphonium nitrate, 1754
Tetramethylammonium chlorite, 1742
Tetramethylammonium pentaperoxodichromate, 3103
Triaminoguanidinium nitrate, 0517

DropBooks

Triethylammonium nitrate, 2580
Uronium nitrate, 0494
See also CHLORITE SALTS

OXYGEN BALANCE

1. Kirk-Othmer, 1965, Vol. 8, 581
2. Slack, R., private comm., 1957

The oxygen balance of a compound is the difference between the oxygen content of the compound and that required fully to oxidise the carbon, hydrogen and other oxidisable elements present to carbon dioxide, water, etc. The concept is of particular importance in the design of explosive compounds or compositions, since the explosive power (energy release) is maximal at equivalence, or zero oxygen balance. If there is a deficiency of oxygen present, the balance is negative, while an excess of oxygen gives a positive balance, and such compounds can function as oxidants. The balance is usually expressed as a percentage. The nitrogen content of a compound is not considered as oxidisable, as it is usually liberated as the gaseous element in explosive decomposition [1].

While it is, then, possible to recognise highly explosive materials by consideration of their molecular formulae and oxygen balance (e.g. ethylene dinitrate, $C_2H_4N_2O_6$ is zero balanced, tetranitromethane, CN_4O_8has +300% balance), the tendency to instability and high energy release becomes apparent well below the balance point. Trinitrotoluene has an oxygen balance of −64%. The empirical statement that the stability of any organic compound is doubtful when the oxygen content approaches that necessary to convert the other elements present to their lowest state of oxidation forms a useful guide [2] in the absence of more specific information. Some examples of oxygen balances may be found in the entries:
Bis(hydrazine)diperchloratochromium(III) perchlorate, 4128
Bis(triperchloratosilicon) oxide, 4190
5-Chloro-1,2,3-thiadiazole, 0655
Hexaamminechromium(III) perchlorate, 4129
Hexaamminecobalt(III) perchlorate, 4126
Mercury(II) oxalate, 0982
Pentaammineaquacobalt(III) chlorate, 4124
Tetraperchloratosilicon, 4169
Titanium tetraperchlorate, 4170
Trinitromethane, 0385

OXYGEN BOMB CALORIMETRY

Plewinsky, B. *et al., Thermochim. Acta*, 1985, **94**, 33–43

Safety aspects of the combustion of various materials in an amosphere of pure oxygen under the conditions prevailing in oxygen bomb calorimetry were investigated experimentally. The combustion of a stable substance (benzoic acid, used to calibrate bomb calorimeters) in oxygen gives a relatively slow combustion, with a low rate of pressure increase of 17 bar/s to a maximum of 64 bar in 2.3 s, for

an initial oxygen pressure of 40 bar, and largely independent of the size of the sample. On the other hand, unstable (or explosive) solids may deflagrate or detonate, leading to very high rates of pressure increase and high maximum pressures, with values very dependent on sample size. Thus, under 40 bar oxygen pressure 0.5 g of picric acid gave values of 3.6 kbar/s to a maximum 98 bar, while 1.5 g gave 54 kbar/s to maximum 216 bar.

In the case of liquid non-explosive samples, three distinct situations can be discerned. First is where the gas phase composition lies outside the explosive range, and rates of pressure rise and maximum pressures attained are both modest and independent of sample size. Examples are benzene and hexamethyldisiloxane, which at 40 bar initial pressure of oxygen gave 36 bar/s to maximum 84 bar, and 63 bar/s to maximum 67 bar, respectively. Second is where the composition of the gas phase lies within the explosive range, as is observed with highly volatile liquids which give a single homogeneous phase, but the explosion pressure and rate of rise strongly depend on the sample size and the initial pressure of oxygen. For a fixed sample size of tetramethyldisiloxane, at an initial oxygen pressure of 10, 15, or 30 bar, rates of rise of 265, 60 and zero kbar/s to maxima of 113, 145 amd zero (no reaction), respectively, were measured. The third case is where the composition of the gas phase is outside the explosive range and the system is heterogeneous (relatively non-volatile liquids), and this has been observed using low initial oxygen pressures with tetramethyldisiloxane and pentamethyldisiloxane.

The former, at 15 bar initial oxygen pressure gave 1 kbar/s rise to 75 bar maximum, but at 20 bar a transition to 21 kbar/s to 121 bar maximum occurs, and at 30 bar to 90 kbar/s and 160 bar maximum is observed, the latter almost certainly involving heterogeneous detonation on the wick and shattering of the containing crucible. Pentamethyldisiloxane at 25 bar initial oxygen pressure shows a rate of rise of 60 bar/s to maximum 49 bar, but at 30 bar initial pressure the rate increases to 38 kbar/s to 205 bar maximum.

PropBooks

See Oxygen (Gas), : Sodium hydroxide, Tetramethyldisiloxane

See other CALORIMETRY

OXYGEN ENRICHMENT

1. *Oxygen Enrichment of Confined Areas*, Information Sheet, Inst. of Welding, 1966
2. Wilk, I. J., *J. Chem. Educ.*, 1968, **45**, A547–551
3. Johnson, J. E. *et al.*, *NRL Rept. 6470*, Washington, Nav. Res. Lab., 1966
4. Woods, F. J. *et al.*, *NRL Rept. 6606*, Washington, Nav. Res. Lab., 1967
5. Denison, D. M. *et al.*, *Nature*, 1968, **218**, 1111–1113
6. Jones, D. A., *Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 1, I13–I22, Rugby, IChE, 1983
7. *NFPA 53M*, Quincy (Na), Natl. Fire Prot. Assocn., 1985
8. ASTM, *STP 1319 (Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres)*, 1997

With the widening availability and industrial use of oxygen, accidents caused by atmospheric enrichment have increased. Most materials, especially clothing, burn

fiercely in an atmosphere containing more than the usual 21 vol% of oxygen. In presence of petroleum products, fire and explosion can be spontaneous. Equipment which may emit or leak oxygen should be used sparingly, and never stored, in confined spaces [1]. Fourteen case histories of accidents caused by oxygen enrichment of the atmosphere are discussed and safety precautions detailed [2]. The flammability of textiles and other solids was studied under the unusual conditions which occur in deep diving operations. The greatest effect on ease of ignition and linear burning rate was caused by oxygen enrichment; increase in pressure had a similar effect [3].

Ignition and flame spread of fabrics and paper were measured at pressures from 21 bar down to the limiting pressure for ignition to occur. Increase in oxygen concentration above 21% in mixtures with nitrogen caused rapid decrease of minimum pressure for ignition. In general, but not invariably, materials ignite less readily but burn faster in helium mixtures than in nitrogen mixtures. The nature of the material has a marked influence on the effect of variables on the rate of burning. At oxygen concentrations of 41% all materials examined would burn except for glass and polytetrafluoroethylene, which resisted ignition attempts in pure oxygen. Flame retardants become ineffective on cotton in atmospheres containing above 32% oxygen [4]. A brief summary of known hazards and information in this general area was published [5]. A method of assessing off-site hazards in the vicinity of bulk liquid oxygen storage installations is presented [6]. The US Fire Protection Association manual covers materials and system design to reduce fire hazards in enriched atmospheres, and includes detail on fire experiences in such systems [7]. The American Society for Testing and Materials has produced an even more comprehensive work [8].

See Oxygen (Gas)

OXYGEN FLUORIDES O_2F, FOF, FOOF, O_2FOF, $(O_2F)_2$

Streng, A. G., *Chem. Rev.*, 1963, **63**, 607

In the series oxygen difluoride, dioxygen difluoride, trioxygen difluoride and tetraoxygen difluoride, as the oxygen content increases, the stability decreases and the oxidising power increases, tetraoxygen difluoride, even at $-200^{\circ}C$, being one of the most potent oxidants known. Applications to both chemical reaction and rocket propulsion systems are covered in some detail.

Individual compounds are:

Dioxygen difluoride, 4320

Hexaoxygen difluoride, 4327

Oxygen difluoride, 4317

'Trioxygen difluoride', 4323

See other HALOGEN OXIDES

OXYGEN INDEX

1. *Oxygen Index Test*, ASTM D2863, 1970
2. Isaacs, J. S., *J. Fire Flamm.*, 1970, **1**, 36–47

3. Kamp, A. C. F. *et al., Proc. 1st Euro. Symp. Therm. Anal.*, 1976, 440–443
4. Redfern, J. P., *Intern. Lab.*, 1979, **9**, 57
5. Kishore, K. *et al., J. Haz. Mat.*, 1980, **3**, 349–356

The flammability properties of volatile materials are readily gauged from the values of the figures for flash point and limits of flammability in air. For involatile flammable materials, a range of empirical tests provides a measure of flammability properties under various circumstances. One of the tests, originally developed to measure the minimum concentration of oxygen in which a sample of a plastics material will continue to burn candle-like, is simple, accurate and reproducible [1]. Results are expressed as an Oxygen Index (O. I.), which is the minimum proportion of oxygen in a mixture with nitrogen to just sustain combustion of a sample of standard size in a chimney-like apparatus. The method has been applied to textile materials [2], and may well be applicable to a much wider range of materials. Determination of the Oxygen Index over a wide temperature range gives a better understanding of flammability parameters, and the Temperature Index (T. I., the temperature at which O. I. is 20.8) will rank flammability of materials. The O. I. at ambient temperature indicates potential hazard at the primary ignition stage, while the T. I. and the O. I.–temperature relation is related to practical fire situations [3]. The mathematical relationships between O. I. and various fire parameters have been reviewed [4]. A new (dimensionless) parameter for flammability of materials, the Flammability Index, is defined in terms of specific heat, flash or autoignition temperature and heat of combustion. It correlates well with the Oxygen Index [5].

1-OXYPEROXY COMPOUNDS O−C−OO−

Swern, 1970,, Vol. 1, 29, 33

This group of compounds includes those monomers with one or more carbon atoms carrying a hydroperoxy or peroxy group, and also singly bonded to an oxygen atom present as hydroxyl, ether or cyclic ether functions. While the group of compounds is, in general, moderately stable, the lower 1-hydroxy and 1,1′-dihydroxy-alkyl peroxides or hydroperoxides are explosive. Individually indexed compounds are:

1-Acetoxy-1-hydroperoxy-6-cyclodecanone, 3669
∗ 1-Acetoxy-6-oxo-cyclodecyl hydroperoxide, 3547
Bis(1-hydroperoxycyclohexyl) peroxide, 3556
Bis(1-hydroxycyclohexyl) peroxide, 3553
Bis(hydroxymethyl) peroxide, 0928
1-Hydroperoxy-1′-hydroxydicyclohexyl peroxide, 3555
∗ 1-Hydroxy-3-butyl hydroperoxide, 1706
Hydroxymethyl hydroperoxide, 0487
Hydroxymethyl methyl peroxide, 0926
∗ 2-Methoxyprop-2-yl hydroperoxide, 1707

OZONIDES

1. Rieche, *Angew. Chem.*, 1958, **70**, 251
2. Swern, 1970, Vol. 1, 39

DropBooks

3. Bailey, P. S., *Chem. Rev.*, 1958, **58**, 928
4. Greenwood, F. L. *et al., J. Org. Chem.*, 1967, **32**, 3373
5. Rieche, A. *et al., Ann.*, 1942, **553**, 187, 224

The preparation, properties and uses of ozonides have been reviewed comprehensively [1]. Many pure ozonides (trioxolanes) are generally stable to storage; some may be distilled under reduced pressure. The presence of other peroxidic impurities is thought to cause the violently explosive decomposition often observed in this group [2]. Use of ozone is not essential for their formation, as they are also produced by dehydration of α,α'-dihydroxy peroxides [3]. A very few isomeric linear trioxides (ROOOR) are known, they are also explosively unstable. Inorganic ozonides, salts of the radical O_{3-} anion, are also hazardous.

Polymeric alkene ozonides are shock-sensitive; that of *trans* -2-butene exploded when exposed to friction in a ground glass joint. The use of GLC to analyse crude ozonisation products is questionable because of the heat-sensitivity of some constituents [4]. Ozonides are decomposed, sometimes explosively, by finely divided palladium, platinum or silver, or by iron(II) salts [5]. Individually indexed compounds are:

Benzene triozonide, 2343
trans-2-Butene ozonide, 1623
† 1,1-Dichloroethylene, Ozone, 0695
1,1-Difluoroethylene ozonide, 0703
1,2-Dimethylcyclopentene ozonide, 2845
∗ 2,5-Dimethyl-2,5-dihydrothiophene-2,5-endoperoxide, 2387
2,6-Dimethyl-2,5-heptadien-4-one diozonide, 3176
2,5-Diphenyl-3,4-benzofuran-2,5-endoperoxide, 3798
Ethylene ozonide, 0836
Fluoroethylene ozonide, 0752
trans-2-Hexene ozonide, 2513
4-Hydroxy-4-methyl-1,6-heptadiene diozonide, 3036
Isoprene diozonide, 1920
Maleic anhydride ozonide, 1406
† 2-Methyl-1,3-butadiene, : Ozone, 1893
3-Methyl-1,2,4-trioxolane, 1235
trans-2-Pentene ozonide, 1982
Pyrocatecholato(2-)(quinolin-8-olato-*N*,*O*)-trioxygenido(2−)phosphorus, 3678
3,3,5-Trifluoro-1,2,4-trioxolane, 0667
Vinyl acetate ozonide, 1543

See also JOJOBA WAX: OZONE

PACKAGING INCIDENTS

Tobias, B. I., *Chem. Eng. News*, 1991, **69**(10), 2

A 500 ml bottle of peracetic acid (ethaneperoxoic acid), provided with a vented cap, was received packed within a tin padded with what appeared to be paper. The metal was distinctly hot to the touch on opening. Peroxyacetic acid is capable of runaway decomposition from 65°C. The heat is thought to have resulted from

seepage through the vent, the bottle having been on its side, followed by reaction with the paper. The importance of inert packing materials is emphasised. Other packaging incidents are:
Acetyl chloride: Water, 0735
Benzenesulfinyl chloride, 2234
Benzenesulfonyl chloride, 2235
Borane–Tetrahydrofuran, 0138
Calcium oxide: Water (reference 5), 3937
Diethyl dicarbonate, 2444
Ethyl oxalyl chloride, 1456
Formic acid, 0418
Nitric acid: Polyalkenes, 4436
Nitric acid: Wood, 4436
Peroxyacetic acid, 0837
Potassium (reference 3), 4645
Pyruvic acid, 1150
Sodium sulfide: Glass, 4811
Trichloromethyl carbonate, 1040
See also INSULATION, PAPER TOWELS

PAINT TAILINGS

See 9,12,15-Octadecatrienoic acid: Cobalt naphthenate

PAPER TOWELS

DropBooks

Unpublished observations, 1970
The increasing use of disposable paper towels and wipes in chemical laboratories accentuates the potential fire hazards arising from the disposal of solid oxidising agents or reactive residues into a bin containing such towels or wipes. The partially wet paper, necessarily of high surface area and absorbency, presents favourable conditions for a fire to be initiated and spread. Separate bins for paper towels etc., and chemical residues seem advisable.
See Zinc: Sodium hydroxide (reference 3)
SODA-LIME
ALDEHYDES, INSULATION, PACKAGING INCIDENTS

PEAT

1. Sansonov, L. N. *et al.*, *Chem. Abs.*, 1988, **109**, 173306
2. Kashinskaya, I. Ya. *et al.*, *Chem. Abs.*, 1989, **110**, 26472

Stockpiles of milled peat are prevented from self heating and ignition by sprayed application of bitumen emulsion to form a 2–2.5 mm protective permeable film [1]. The mechanism of self heating and ignition first involves aerobic microbiological processes, then chemical transformation of iron-containing minerals in the peat into pyrophoric iron compounds which later ignite the peat mound [2].

PYROPHORIC IRON–SULFUR COMPOUNDS
DUST EXPLOSION INCIDENTS (reference 21)

PENTAAZADIENES **ArN=NNRN=NAr**

See Bis[1,5-bis(4-methylphenyl)-1,3-pentazadienato-N3,N5]-(T-4) cobalt
See TRIAZENES (reference 3) *See other* HIGH-NITROGEN COMPOUNDS

N–PENTAFLUOROSULFUR COMPOUNDS **R_2NSF_5**

1. Sitzmann, E., *Chem. Abs.*, 1992, **116**, 132303z
2. De Yong, L. V. *et al., Chem. Abs.*, 1993, **119**, 142309g

A series of carbonimidate esters bearing a pentafluorosulfur group on the nitrogen are described as explosives. The SF_5 is unlikely to be ornamental although most of the alkoxy groups involved also carry nitro groups [1]. However, another study of explosives which bore a pentafluorothio group, probably on carbon, suggested it was equivalent to an hydrogen [2].

PERCHLORATE-DOPED CONDUCTING POLYMERS

1. Eisenbaumer, R. L.. *et al., Chem. & Eng. News*, 1985, **63**(22), 4
2. Young, X.-Z. *et al., J. Polymer Sci. (Polymer Chem. Edn.*), 1985, **23**, 859
3. Varyu, M. E. *et al., Chem. & Eng. News*, 1985, **63**(24), 4
4. Österholm, J.-E. *et al., Chem. & Eng. News*, 1986, **64**(6), 2
5. Druy, M. A., *Chem. Eng. News*, 1986, **64**(12), 2
6. Julia, L. *et al., Chem. & Ind.*, 1989, 78–79
7. Editor's comments

A piece of poly(acetylene) film doped with perchlorate detonated spontaneously inside an argon-filled dry box. Doping had been effected by contacting the film with a solution of iron(III) perchlorate in toluene–nitromethane, followed by washing and high-vacuum drying. Samples of the doped film had previously been tested and showed no signs of instability under impact, physical stress, or on flame contact. The explosion occurred 2 weeks later when further samples were being taken [1]. A sample of similar material undergoing thermogravimetric analysis had exploded at 160°C [2]. Use of electrochemical (rather than chemical) doping methods is preferred as more controlable, with determination of perchlorate content (as chloride) by oxygen flask combustion analysis. Limitation of analytical sample size to 10 mg and other precautions are recommended [3]. Perchlorate-doped poly(thiophene) film (up to 25–30 mol % of perchlorate in the matrix) has also been prepared and found stable under ambient conditions. However it is extremely unstable at temperatures above 100°C (possibly explosive), and samples of film intensively desiccated over phosphorus pentaoxide have exploded on handling with tweezers. Great care is necessary in handling such materials [4]. Perchlorate-doped poly(pyrrole) and poly(thiophene) film in a dry atmosphere tend to explode when handled with tweezers, though such films were stable to heating at above 100°C. Trifluoromethanesulfonate and *p*-toluenesulfonate are more suitable doping

counterions than perchlorate [5]. The use of thallium(III) trifluoroacetate in trifluoroacetic acid as combined oxidant and dopant appears to give stable radical ion salts of poly(thiophene) [6].

Some conducting polymers with a conjugated polyvinyl structure, such as polyacetylene and poly(phenylacetylene), seem likely to be energetic enough, and reactive enough, to give trouble undoped, if they actually have the supposed structure [7].

See related NON-METAL PERCHLORATES

See Ethylene, Butadiene, Styrene

PERCHLORATES —$OClO_3$

1. Schumacher, 1960
2. Burton, H. *et al., Analyst,* 1955, **80**, 4

All perchlorates have some potential for hazard when in contact with other mutually reactive materials, while many are intrinsically hazardous, owing to the high oxygen content.

Existing knowledge on perchloric acid and its salts was reviewed extensively in 1960 in a monograph including the chapters: Perchloric Acid; Alkali Metal, Ammonium and Alkaline Earth Perchlorates; Miscellaneous Perchlorates; Manufacture of Perchloric Acid and Perchlorates; Analytical Chemistry of Perchlorates; Perchlorates in Explosives and Propellants; Miscellaneous Uses of Perchlorates; Safety Considerations in Handling Perchlorates [1]. There is a shorter earlier review, with a detailed treatment of the potentially catastrophic acetic anhydride–acetic acid–perchloric acid system. The violently explosive properties of methyl, ethyl and lower alkyl perchlorate esters, and the likelihood of their formation in alcohol–perchloric acid systems, are stressed. The instability of diazonium perchlorates, some when damp, is discussed [2].

DropBooks

The class has been divided into the separately treated groups:

ALKYL PERCHLORATES, AMMINEMETAL OXOSALTS
AMINIUM PERCHLORATES, DIAZONIUM PERCHLORATES
METAL PERCHLORATES, NON-METAL PERCHLORATES
PERCHLORATE SALTS OF NITROGENOUS BASES

Glycol, Polymer

MCA Case History No. 464

A mixture of an inorganic perchlorate salt, a glycol and a polymer exploded violently after heating at 265–270°C. It was thought that the glycol may have been oxidised, but formation of the glycol perchlorate ester(s) seems a likely alternative cause.

Organic matter

Schumacher, 1960, 188

Mixtures of perchlorate salts with finely divided or fibrous organic materials are likely to be explosive. Porous or fibrous materials exposed to aqueous solutions and then dried are rendered explosively flammable and are easily ignited.

Reducants

1. Mellor, 1941, Vol. 2, 387; Vol. 3, 651
2. Schumacher, 1960, 188

Perchlorate salts react explosively when rubbed in a mortar with calcium hydride or with sulfur and charcoal, when melted with reducants, or on contact with glowing charcoal [1]. Mixtures with finely divided aluminium, magnesium, zinc or other metals are explosives [2].

See other REDOX REACTIONS

PERCHLORATE SALTS OF NITROGENOUS BASES $N^+ ClO_4^-$

Kozak, G. D. *et al., Chem. Abs.,* 1981, **94**, 86609

In a study of detonation of aqueous solutions of perchlorate salts of hydroxylamine, urea, methylamine and diaminoethane (mono- or di-salts), the former could be detonated in 20−25% solution at 407−587°C.

Many other perchlorate salts of nitrogenous bases have been involved in explosive incidents, individually indexed compounds being:

2-Aminoethylammonium perchlorate, 0958
Ammonium perchlorate, 4004
Anilinium perchlorate, 2367
2-Aza-1,3-dioxolanium perchlorate, 0898
∗ 2-Azatricyclo[2.2.1.$0^{2,6}$]hept-7-yl perchlorate, 2368
∗ 1,4-Bis(2-chloroethyl)-1,4-bis(azonia)bicyclo[2.2.1]heptane periodate, 3192
1,2-Bis(ethylammonio)ethane perchlorate, 2589
Chloroformamidinium perchlorate, 0469
Dimethylammonium perchlorate, 0950
1,3-Dimethyl-2,1-benzisoxazolium perchlorate, 3148
1,1-Dimethyldiazenium perchlorate, 0938
1-(4,5-Dimethyl-1,3-diselenonylidene)piperidinium perchlorate, 3340
2,2-Dimethyltriazanium perchlorate, 0963
2,4-Dinitrophenylhydrazinium perchlorate, 2351
N,N-Diphenyl-3-phenylpropenylidenimmonium perchlorate, 3820
2-(1,3-Diselena-4,5,6,7-tetrahydroindanylidene)piperidinium perchlorate, 3408
1,2-Ethylenebis(ammonium) perchlorate, 0964
Guanidinium perchlorate, 0502
Hydrazinium diperchlorate, 4068
Hydrazinium perchlorate, 4011
2-Hydroxyethylaminium perchlorate, 0951
Hydroxylaminium perchlorate, 4005
Methylammonium perchlorate, 0501
1-(4-Methyl-1,3-diselenonylidene)piperidinium perchlorate, 3174
1-Methyl-3-nitroguanidinium perchlorate, 0939
Morpholinium perchlorate, 1680
4-Nitroanilinium perchlorate, 2350
Perchloric acid, : Nitrogenous epoxides, 3998
∗ Phosphonium perchlorate, 4006

Poly(dimercuryimmonium perchlorate), 4012
Pyridinium perchlorate, 1863
Tetraethylammonium perchlorate, 3088
Tetrafluoroammonium perchlorate, 3986
N,N,N′,N′-Tetramethylformamidinium perchlorate, 2026
Triaminoguanidinium perchlorate, 0515
Trimethylammonium perchlorate, 1322
Trimethylhydroxylammonium perchlorate, 1323
Tri(4-tolyl)ammonium perchlorate, 3824
Uronium perchlorate, 0491

PERCHLORYLAMIDE SALTS $M^+ (O_3ClNH)^-$

1. *Perchloryl Fluoride*, Booklet DC-1819, Philadelphia, Pennsalt Chem. Corp., 1957
2. Hennrichs, W. *et al., Z. Anorg. Chem.*, 1983, **50** 6, 205

Ammonium perchlorylamide and the corresponding silver and barium salts are shock-sensitive when dry and may detonate. Extreme care is required when handling such salts [1]. Some *N*-benzylperchlorylamide derivatives are also unstable, and the barium, silver and mercury salts explode on impact, and the two latter on heating to 105 and 120°C, respectively [2].

Individually indexed compounds are:
Ammonium perchlorylamide, 4009
Barium perchlorylamide, 0203
Barium *N*-perchlorylbenzylamide, 3649
Mercury(II) *N*-perchlorylbenzylamide, 3651
Monopotassium perchlorylamide, 3994
Potassium perchlorylamide, 4019
Silver perchlorylamide, 0028
Silver *N*-perchlorylbenzylamide, 2734
See other PERCHLORYL COMPOUNDS, *N*-METAL DERIVATIVES

DropBooks

PERCHLORYL COMPOUNDS $RNHClO_3$, $ArClO_3$

1. *Friedel-Crafts and Related Reactions*, Olah, G. A. (Ed.), Vol. 3.2, 1507–1516, New York, Interscience, 1964
2. Baum, K. *et al., J. Amer. Chem. Soc.*, 1974, **96**, 3233–3237
3. Beard, C. D. *et al., J. Amer. Chem. Soc.*, 1974, **96**, 3237–3239

The need for great care to avoid the possibility of detonation of perchloryl compounds by exposure to shock, overheating or sparks is stressed. The compounds are generally more sensitive to impact than mercury fulminate and are of comparable sensitivity to lead azide [1]. A range of highly explosive alkyl perchlorates [2] and perchlorylamines [3] have been prepared by interaction of dichlorine heptaoxide with alcohols or amines in carbon tetrachloride solution. The solutions of the products were not sensitive to mechanical shock and could

be used directly for further reactions. Adequate warning of the explosion hazards involved in isolating perchloryl compounds is given.

Individually indexed compounds are:
2,6-Dinitro-4-perchlorylphenol, 2101
2,6-Diperchloryl-4,4′-diphenoquinone, 3444
3-Nitroperchlorylbenzene, 2143
Perchlorylbenzene, 2236
Perchloryl fluoride, 3974
N-Perchlorylpiperidine, 1949
See also PERCHLORYLAMIDE SALTS

PERFLUOROSILANES **Si_mF_n**

Bailar, 1973, Vol. 1, 1385
The compounds in this group (Si_2F_6 to Si_4F_{10} are mentioned later) are said to ignite in air and react violently with water.
See other HALOSILANES

PEROXIDATION INCIDENTS

Many incidents involving explosions have been attributed, not always correctly, to peroxide formation and violent decomposition. Individually indexed incidents are:
2-Acetyl-3-methyl-4,5-dihydrothiophen-4-one, 2807
Aluminium dichloride hydride diethyl etherate, : Dibenzyl ether, 0061
† 1,3-Butadiene, 1480
† Diallyl ether, 2431
† Diisopropyl ether, 2542
Lithium tetrahydroaluminate, : Tetrahydrofuran, 0075
Peroxyacetic acid, : Ether solvents, 0837
† 2-Propen-1-ol, : Sulfuric acid 1.42/53, 1223
Sulfinyl chloride, : Diisopropyl malonate, 4096
See PEROXIDES IN SOLVENTS, PEROXIDISABLE COMPOUNDS
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

PEROXIDES **−OO−**

This class name covers one of the largest classes of hazardous compounds, with 3 main divisions: these groups are further subdivided for convenience.

INORGANIC PEROXIDES
ORGANIC PEROXIDES
ORGANOMETALLIC PEROXIDES

PEROXIDES IN SOLVENTS

1. Author's comments, 1984
2. Burfield, D. R., *J. Org. Chem.*, 1982, **47**, 3821–3824

Many laboratory accidents have been ascribed to presence of peroxides in solvents, usually, but not exclusively ethers. Storage of the solvents for over-long periods,

often under poor conditions, is a common feature of the incidents. When peroxides are removed from solvents by chromatographic adsorption on alumina columns, the concentrated band of strongly adsorbed peroxides at the top of the column may become hazardous if the solvent evaporates [1]. The use of self-indicating molecular sieve under nitrogen is described as an effective method of de-peroxidising THF, diethyl and dipropyl ethers, suitable also for bulk-scale operations [2].

See ETHERS
PEROXIDE TEST STRIPS
PEROXIDISABLE COMPOUNDS
2-Butanol, 1695
2-Butanone, 1606
Diethyl ether, 1697
Diisopropyl ether, 2542
1,4-Dioxane, 1617
4-Methyl-2-pentanone, 2495
2-Propanol, 1280
Tetrahydrofuran, 1612
Hydrogen peroxide: Acetone, 4477
Peroxomonosulfuric acid: Acetone, 4481

PEROXIDE TEST STRIPS

See 1-Allyloxy-2,3-epoxypropane
See also PEROXIDES IN SOLVENTS

DropBooks

PEROXIDISABLE COMPOUNDS

1. Jackson, H. L. *et al., J. Chem. Educ.*, 1970, **47**, A175
2. Brandsma, 1971, 13
3. *MCA Case History No. 1693*
4. *Recognition and Handling of Peroxidisable Compounds*, Data sheet 1-655, Chicago, National Safety Council, 1982
5. Shanley, E. S., *Chem. Eng. News*, 1979, **57**(21), 43
6. Mirafzal, G. A. *et al., J. Chem. Educ.*, 1988, **65**(9), A226–229
7. Bretherick, L., private comm. to Dr Mirafzal, 1988; *J. Chem. Educ.*, 1990, **67**(9), A230
8. Kelly, R. J., *Chem. Health & Safety*, 1996, **3**(5), 28

An account of a Du Pont safety study of the control of peroxidisable compounds covers examples of peroxidisable structures, handling procedures, distillation of peroxidisable compounds, and detection and elimination of peroxides [1]. Essential organic structural features for a peroxidisable hydrogen atom are recognised as those below. While the two structural types at the end of that list readily peroxidise, in some cases the products are readily degradable and do not accumulate to a hazardous level. A notable exception is acetaldehyde which is converted to peroxyacetic acid. Inorganic compounds which readily peroxidise are listed as potassium (which gives the superoxide) and higher alkali metals, alkali metal alkoxides and amides, and organometallic compounds.

Three lists of specific compounds or compound types indicate different types of potential hazard, and appropriate storage, handling and disposal procedures are detailed for each.

List A, giving examples of compounds which form explosive peroxides while in storage, include diisopropyl ether, divinylacetylene, vinylidene chloride, potassium and sodium amide. Review of stocks and testing for peroxide content by given tested procedures at 3-monthly intervals is recommended, together with safe disposal of any peroxidic samples.

List B, giving examples of liquids where a degree of concentration is necessary before hazardous levels of peroxides will develop, includes several common solvents containing one ether function (diethyl ether, ethyl vinyl ether, tetrahydrofuran), or two ether functions (*p*-dioxane, 1,1-diethoxyethane, the dimethyl ethers of ethylene glycol or 'diethylene glycol'), the secondary alcohols 2-propanol and 2-butanol, as well as the susceptible hydrocarbons propyne, butadiyne, dicyclopentadiene, cyclohexene and tetra- and deca-hydronaphthalenes. Checking stocks at 12 monthly intervals, with peroxidic samples being discarded or repurified, is recommended here [1].

A simple method of effectively preventing accumulation of dangerously high concentrations of peroxidic species in distillation residues is that detailed in an outstanding practical textbook of preparative acetylene chemistry [2]. The material to be distilled is mixed with an equal volume of non-volatile mineral oil. This remains after distillation as an inert diluent for polymeric peroxidic materials.

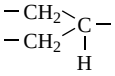
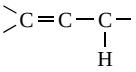
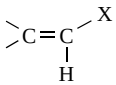
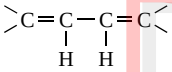
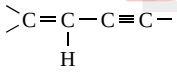
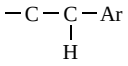
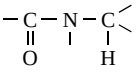
List C contains peroxidisable monomers, where the presence of peroxide may initiate exothermic polymerisation of the bulk of material. Precautions and procedures for storage and use of monomers with or without the presence of inhibitors are discussed in detail. Examples cited are acrylic acid, acrylonitrile, butadiene, 2-chlorobutadiene, chlorotrifluoroethylene, methyl methacrylate, styrene, tetrafluoroethylene, vinyl acetate, vinylacetylene, vinyl chloride, vinylidene chloride and vinylpyridine [1].

In general terms, the presence of two or more of the structural features indicated above in the same compound will tend to increase the risk. The selection of compound groups and of individually indexed compounds below includes compounds known to have been involved or those with a multiplicity of such structural features which would be expected to be especially susceptible to peroxide formation. A more recent and thorough review of peroxidation risks gives a critical assessment of test methods for peroxides [8].

Subsequent to incidents involving peroxidation of stored bottles of vinylidene chloride, a labelling procedure and list of peroxidisable compounds was prepared [3]. Of the 108 compounds listed, 35 are noted as forming peroxides with ease, and these need particular care in storage and use. A revised data sheet is now available [4], and peroxide-containing residues may often be rendered innocuous by pouring into an excess of sodium carbonate solution [5].

The argument in an addendum to reference 1 above which claims that primary alcohols should also be classed as peroxidisable [6] is flawed. Among the primary alcohols listed as peroxide formers, the structures of those which formed significant levels of peroxide in storage all possessed tertiary H atoms susceptible to

autoxidation by virtue of their position on the branched carbon skeletons of the alcohols, as well as the (insusceptible) primary hydroxyl group. While it is true that secondary alcohols should certainly be added to List B above, it is not necessary for primary alcohols as such, unless the structure is branched, when there may be susceptible hydrogen(s) present to warrant caution. It is the nature of the carbon skeleton, rather than presence of the hydroxyl group, which is the more important factor [7].

BOND GROUPINGS	*CLASS ENTRY*
	as in acetals, ethers, oxygen heterocycles
	as in isopropyl compounds, decahydronaphthalenes
	as in allyl compounds
	as in haloalkenes
	as in other vinyl compounds (Monomeric esters, ethers, etc.)
	as in dienes
	as in vinylacetylenes
	as in cumenes, tetrahydronaphthalenes, styrenes
	as in aldehydes
	as in *N*-alkyl-amides or -ureas, lactams

DropBooks

See Indane-2-aldehyde

ACETYLENIC COMPOUNDS, ALKALI METALS
ALKENES, ALKYNES
BENZYL COMPOUNDS, DIENES
HALOALKENES, OXIMES
TETRAHYDROPYRANYL ETHER DERIVATIVES

and individually indexed compounds:

† Acetaldehyde, 0828
† Acrylaldehyde, 1145
† Allyl ethyl ether, 1955
1-Allyloxy-2,3-epoxypropane, 2434
† Bis(2-ethoxyethyl) ether, 3076
Bis-(2-methoxyethyl) ether, 2549
† 1,3-Butadiene, 1480
† 1,3-Butadiyne, 1385
† 2-Butanol, 1695
† Buten-3-yne, 1423
† Butyl ethyl ether, 2540
† Butyl vinyl ether, 2484
† 2-Chloro-1,3-butadiene, 1451
† Chloroethylene, 0730
† 2-Chloroethyl vinyl ether, 1557
Cinnamaldehyde, 3134
† Crotonaldehyde, 1516
† Cyclopropyl methyl ether, 1608
† Diallyl ether, 2431
Dibenzyl ether, 3655
† Dibutyl ether, 3071
† 1,1-Dichloroethylene, 0695
† 1,1-Diethoxyethane, 2545
† 1,2-Diethoxyethane, 2546
† 3,3-Diethoxypropene, 2858
† Diethyl ether, 1697
Diethylketene, 2430
† 2,3-Dihydrofuran, 1517
† Diisopropyl ether, 2542
† 1,1-Dimethoxyethane, 1700
† 1,2-Dimethoxyethane, 1701
† Dimethoxymethane, 1281
† 3,3-Dimethoxypropene, 1968
† 1,3-Dioxane, 1616
† 1,4-Dioxane, 1617
∗ 1,3-Dioxol-4-en-2-one, 1087
† Dipropyl ether, 2543
Di(2-propynyl) ether, 2327
† Divinyl ether, 1519
2-Ethoxyethanol, 1702
1-Ethoxy-2-propyne, 1909
2-Ethylacryladehyde oxime, 1933
† 2-Ethylbutanal, 2487
† 2-Ethylhexanal, 3050
† Ethyl isopropyl ether, 2012
† Ethyl propenyl ether, 1956

† Ethyl vinyl ether, 1610
2-Furaldehyde, 1836
† Furan, 1439
2,4-Hexadienal, 2383
4,5-Hexadien-2-yn-1-ol, 2328
2,5-Hexadiyn-1-ol, 2329
2-Hexenal, 2432
2-Indanecarboxaldehyde, 3288
† Isobutyraldehyde, 1611
2-Isopropylacrylaldehyde oxime, 2453
† Isopropyl vinyl ether, 1957
† Isovaleraldehyde, 1958
Limonene, 3337
1,5-*p*-Menthadiene, 3338
∗ Methoxy-1,3,5,7-cyclooctatetraene, 3149
2-Methoxyethanol, 1284
† 2-Methoxyethyl vinyl ether, 1973
∗ 2-(1-Methylheptyl)-4,6-dinitrophenyl crotonate, 3764
† 2-3-Methyl-2-methylenebutanal, 2433
† 4-Methyl-2-pentanone, 2495
† 2-Methyltetrahydrofuran, 1961
† Methyl vinyl ether, 1221
α -Pentylcinnamaldehyde, 3663
† Propionaldehyde, 1224
Sodium 5,8,11,14-eicosatetraenoate, 3809
Sodium ethoxyacetylide, 1478
1,1,2,3-Tetrachloro-1,3-butadiene, 1389
† Tetrahydrofuran, 1612
Tetrahydronaphthalene, 3300
† Tetrahydropyran, 1965
Tridecanal, 3619
† Vinyl acetate, 1532
† 4-Vinylcyclohexene, 3004

DropBooks

PEROXOACIDS **EOOH**

Inorganic acids with a peroxide function are given the IUPAC name above, which distinguishes them from the organic PEROXYACIDS. Collectively they are a group of very powerful oxidants, individual compounds being:
Peroxodisulfuric acid, 4482
Peroxomonophosphoric acid, 4506
Peroxomonosulfuric acid, 4481
Peroxonitric acid, 4437

Many of the salts of peroxoacids are unstable or explosive, are capable of initiation by heat, friction or impact, and all are powerful oxidants. Individually indexed compounds are:

Ammonium hydroxyoxodiperoxochromate(1−), 4230
Ammonium pentaperoxodichromate(2−), 4247
Ammonium peroxoborate, 0146
Ammonium peroxodisulfate, 4576
Ammonium tetraperoxochromate(1−)
Calcium peroxodisulfate, 3940
Calcium triperoxochromate, 3945
Mercury(II) peroxybenzoate, 3637
Potassium *O*−*O*-benzoylmonoperoxosulfate, 2684
Potassium diperoxomolybdate, 4659
Potassium diperoxoorthovanadate, 4667
Potassium hydrogen peroxomonosulfate, 4430
Potassium hydroxyoxodiperoxochromate(1−), 4227
Potassium pentaperoxodichromate, 4249
Potassium peroxodisulfate, 4668
Potassium peroxoferrate(2−), 4396
Potassium tetraperoxochromate(3−), 4235
Potassium tetraperoxomolybdate, 4660
Potassium tetraperoxotungstate, 4669
Potassium tricyanodiperoxochromate(3−), 1044
Silver peroxochromate, 0037
Sodium monoperoxycarbonate, 0554
Sodium peroxoborate, 0155
Sodium peroxodisulfate, 4809
Sodium peroxyacetate, 0780
Sodium peroxydicarbonate, 1024
Sodium tetraperoxochromate(3−), 4240
Sodium tetraperoxomolybdate, 4715
Sodium tetraperoxotungstate, 4810
Tetramethylammonium pentaperoxodichromate, 3103
Thallium hydroxyoxodiperoxochromate(1−), 4228
Thallium(I) peroxodiborate, 0171

See other OXIDANTS

PEROXOCHROMIUM COMPOUNDS

1. Pope, M. T. *et al.*, *Chem. Rev.*, 1994, **94**(3), 576
2. Editor's comments

Most solid peroxochromates explode when heated or struck, some are reported to explode spontaneously at room temperature. Few have been isolated and fully characterised. Assigned structures are sometimes doubtful [1], especially when questionable primary sources have been reinterpreted by secondary and tertiary

reviews. A wide and confused selection of peroxochromate salts is to be found in the literature. It seems probable that there are, in fact, only two main series: the red tetraperoxochromate(3−) salts most of which explode only when provoked by heat or strong acid, and those of a more sensitive blue mono-anion, probably hydroxyoxodiperoxychromate(1−) which just explode. The latter series have an anhydride, CrO_5, which may be isolated as relatively stable complexes with electron donors such as methanol or pyridine. Both series are made by treating chromium(VI) species with hydrogen peroxide, at differing pH, and may be interconverted [2]. There is also a mostly neutral group, generally shock and heat sensitive, of diperoxochromium compounds with three donor ligands [1]. A great many others will be found in this work, mostly the result of mistaken identity due to poor analysis. For individual peroxochromate salts and neutral complexes:

Diammonium Aquabis(peroxotartratovanadate)(2−), 3079

See entries PEROXOACID SALTS, AMMINECHROMIUM PEROXOCOMPLEXES

PEROXOMOLYBDATES AND TUNGSTATES

Pope, M. T. *et al.*, *Chem. Rev.*, 1994, **94**(3), 576

Most tetraoperoxomolybdates(2−) and tetraperoxotungstates(2−) explode when heated or struck. For individual salts:

Diammonium Aquabis(peroxotartratovanadate)(2−)

See entry PEROXOACID SALTS

PEROXYACIDS RCO.OOH

1. Castrantas, 1965, 12; Swern, 1970, Vol. 1, 59, 337
2. Isard, A. *et al.*, Ger. Offen., 1 643 158, 1968
3. Isard, A. *et al.*, *Chemical Tech.*, 1974, **4**, 380
4. Swern, D., *Chem. Rev.*, 1945, **45**, 3−16
5. Augustine, 1969, 221, 217
6. Payne, G. B., *J. Org. Chem.*, 1962, **27**, 628
7. Augustine, 1971, 164

The peroxyacids were until relatively recently the most powerful oxidants of all organic peroxides, and it is often unnecessary to isolate them from the mixture of carboxylic acid and hydrogen peroxide used to generate them. The pure lower aliphatic members are explosive (performic, particularly) at high, but not low concentrations, being sensitive to heat but not usually to shock. Dipicolinic acid or phosphates have been used to stabilise these solutions. The detonable limits of peroxyacid solutions can be plotted by extrapolation from known data. Aromatic peroxyacids are generally more stable, particularly if ring substituents are present [1].

The patented preparation of peroxyacids [2] by interaction of carboxylic acids with hydrogen peroxide in presence of metaboric acid needs appropriate safeguards to prevent accidental separation of the conc. peroxyacids [3]. Much descriptive data on stabilities of a wide selection of peroxyacids has been summarised [4]. A general method of preparation of peroxyacids involving addition of e.g. the anhydrides of acetic, maleic, phthalic or trifluoroacetic acids to a suspension of 90%

DropBooks

hydrogen peroxide in dichloromethane with a drop of sulfuric acid, which although it contravenes the rule of adding concentrated hydrogen peroxide to the substrate (rather than the reverse), is nevertheless preferred because it minimises handling of concentrated peroxide, and avoids the possibility of its contact with stopcock grease [5]. However, the mixture of 90% hydrogen peroxide and dichloromethane is reported to be shock-sensitive [6]. In metal-ion catalysed oxidations by peroxyacids, it is necessary to avoid metal catalysed decomposition of the peroxy acid. Traces of transition metal ions (cobalt, iron, manganese, nickel or vanadium) can lead to explosively violent decomposition of lower aliphatic peroxyacids (peroxyformic, -acetic, -pivalic, -trifluoroacetic acids), even at concentrations of 25% in inert solvents. Maintenance of high-dilution conditions will prevent such runaway reactions [7]. Individually indexed peroxyacids are:

Benzeneperoxyseleninic acid, 2337
Benzeneperoxysulfonic acid, 2341
3-Chloroperoxybenzoic acid, 2676
Diperoxyazelaic acid, 3189
Diperoxyterephthalic acid, 2925
Monoperoxysuccinic acid, 1542
Peroxyacetic acid, 0837
Peroxybenzoic acid, 2733
3-Peroxycamphoric acid, 3348
Peroxycrotonic acid, 1535
Peroxyformic acid, 0420
Peroxyfuroic acid, 1837
Peroxyhexanoic acid, 2514
Peroxypropionic acid, 1236
Peroxytrifluoroacetic acid, 0666
Trichloroperoxyacetic acid, 0659

See *1,1*-DI(BENZOYLPEROXY)ARYLIODINES
POLYMERIC PEROXYACIDS
ORGANIC PEROXIDES

PEROXYCARBONATE ESTERS −OCO.OOR, −OOCO.OOR

1. Strain, F. *et al., J. Amer. Chem. Soc.*, 1950, **72**, 1254
2. Kirk-Othmer, 1967, Vol. 14, 803

Of the 3 possible types of peroxycarbonate esters−dialkyl monoperoxycarbonates, dialkyl diperoxycarbonates and dialkyl peroxydicarbonates−, the latter are by far the least stable group. Several of the 16 alkyl and substituted-alkyl esters prepared decomposed violently or explosively at temperatures only slightly above the temperature of preparation (0−10°C), owing to self-accelerating exothermic decomposition. Several were also explosive on exposure to heat, friction or shock [1]. Amines and certain metals cause accelerated decomposition of dialkyl peroxydicarbonates by a true catalytic mechanism [2]. Individually indexed compounds are:

O−*O*-*tert*-Butyl isopropyl monoperoxycarbonate, 3051
Bis(2-methoxyethyl) peroxydicarbonate, 3037
Diallyl peroxydicarbonate, 2989
Di-*tert*-butyl diperoxycarbonate, 3194
Didodecyl peroxydicarbonate, 3865
Diethyl peroxydicarbonate, 2446
Diisopropyl peroxydicarbonate, 3034
Dimethyl peroxydicarbonate, 1544
Dipropyl peroxydicarbonate, 3035
See other PEROXIDES

PEROXY COMPOUNDS **C−OO−**

Castrantas, 1965
Detonation theory is used to clarify the explosive characteristics of peroxy compounds. Some typical accidents are described. Hazards involved in the use of a large number of peroxy compounds (including all those then commercially available) are tabulated, with 134 references.

PEROXYESTERS **−CO.OOR**

Castrantas, 1965, 13; Swern, 1970, Vol. 1, 79
Although as a group the peroxyesters are noted for instability, there is a fairly wide variation in stability between particular sub-groups and compounds.
See tert-BUTYL PEROXOPHOSPHATE DERIVATIVES
1,1-DI(BENZOYLPEROXY)ARYLIODINES
PEROXYCARBONATE ESTERS

DropBooks

and the individually indexed compounds:
1,1-Bis(benzoylperoxy)cyclohexane, 3804
1,1-Bis(4-nitrobenzoylperoxy)cyclohexane, 3800
Bis(trimethylsilyl) peroxomonosulfate, 2602
tert-Butyl 1-adamantaneperoxycarboxylate, 3692
tert-Butyl chloroperoxyformate, 1926
tert-Butyl diperoxyoxalate, 3356
O−*O*-*tert*-Butyl hydrogen monoperoxymaleate, 3015
tert-Butyl 4-nitroperoxybenzoate, 3400
tert-Butyl peroxyacetate, 2509
† *tert*-Butyl peroxybenzoate, 3401
∗ Butyryl peroxonitrate, 1574
tert-Butyl peroxynitrate, 1663
Di-*tert*-butyl diperoxycarbonate, 3194
Di-*tert*-butyl diperoxyphthalate, 3715
† 1,1-Dichloroethyl peroxyacetate, 1491
Fluorocarbonylperoxonitrate, 0338
1-Hydroxyethyl peroxyacetate, 1626
† Isobutyl peroxyacetate, 2512

∗ Pentafluorosulfur peroxyacetate, 0755
∗ Peroxyacetyl nitrate, 0766
∗ Peroxyacetyl perchlorate, 0737
∗ Peroxypropionyl nitrate, 1187
∗ Poly(peroxyisobutyrolactone), 1536
1,1,6,6-Tetrakis(acetylperoxy)cyclododecane, 3810
7,7,10,10-Tetramethyl-1,2,5,6-tetroxecane-3,4-dione, 3349
Trichloromethyl peroxyacetate, 1097
Trifluoromethyl 3-fluorocarbonylhexafluoroperoxybutyrate, 2061
Trifluoromethyl peroxonitrate, 0346
Trifluoromethyl peroxyacetate, 1103

PETROLEUM COKE

1. Hulisz, S., *Chem. Abs.*, 1977, **86**, 19269
2. Statkov, O. P. *et al., Chem. Abs.*, 1989, **110**, 62453

The flammability and explosivity of high-sulfur petroleum coke dust (particle size <75 μm) were examined. Air-dried powder was non-explosive but fire-prone above 400°C. A 5 mm layer became incandescent at 420−470° and a dust cloud ignited at 520−660°C [1]. The fire and explosion hazards of petroleum coke or anthracite, when used in the manufacture of furnace electrodes, may be reduced by heat treatment [2].

See CARBON, *also* CARBONACEOUS DUSTS

α-PHENYLAZO HYDROPEROXIDES −C(OOH)N=NPh

1. Swern, 1971, Vol. 2, 19
2. Busch, M. *et al., Ber.*, 1914, **47**, 3277
3. Baumstark, A. L. *et al., J. Org. Chem.*, 1983, **48620, 69**
4. Tezuka, T. *et al., J. Chem. Soc., Perkin Trans. 1*, 1984, 2509
5. Tezuka, T. *et al., Chem. Lett.*, 1986, 1671−1674

Alkyl- and aryl-hydrazones of aldehydes and ketones readily peroxidise in solution and rearrange to azo hydroperoxides [1], some of which are explosively unstable [2]. Dry samples of the *p*-bromo- and *p*-fluoro-hydroperoxybenzylazobenzenes, prepared by oxygenation of benzene solutions of the phenylhydrazones, exploded while on filter paper in the dark, initiated by vibration of the table or tapping the paper. Samples were later stored moist with benzene at −60°C to prevent explosion [3]. A series of α-phenylazo hydroperoxides derived from the phenyl- or *p*-bromophenyl-hydrazones of acetone, acetophenone or cyclohexanone, and useful for epoxidation of alkenes, are all explosive [4]. The stability of several substituted phenylazo hydroperoxides was found to be strongly controlled by novel substituent effects [5].

Individually indexed compounds are:
α-(4-Bromophenylazo)benzyl hydroperoxide, 3606
α-(4-Bromophenylazo)phenylethyl α-hydroperoxide, 3648

2-(4-Bromophenylazo)-2-propyl hydroperoxide, 3156
1,2-Dihydroperoxy-1,2-bis(benzeneazo)cyclohexane, 3762
α-Phenylazobenzyl hydroperoxide, 3609
α-Phenylazo-4-bromobenzyl hydroperoxide, 3607
1-Phenylazocyclohexyl hydroperoxide, 3539
α-Phenylazo-4-fluorobenzyl hydroperoxide, 3608
∗ 3,3,5-Triphenyl-4,4-dimethyl-5-hydroperoxy-4,5-dihydro(3H)pyrazole, 3841

PHOSPHINES RPH_2, R_2PH

Halogens
Van Wazer, 1958, Vol. 1, 196
Organic derivatives of phosphine react very vigorously with halogens

Individually indexed (unsubstituted) phosphines are:
∗ Cobalt tris(dihydrogenphosphide), 4203
∗ *N,N′*-Di-*tert*-butyl-*N,N′*-bis(trimethylsilyl)diaminophosphene, 3675
† Diphosphane, 4538
∗ Potassium dihydrogenphosphide, 4460
∗ Sodium dihydrogen phosphide, 4474
∗ Tetrakis(trimethylsilyl)diaminodiphosphene, 3588
∗ Trimethylgermylphosphine, 1332
∗ Tris(iodomercurio)phosphine, 4614
∗ Trisilylphosphine, 4583
∗ *N,N,N′*-Tris(trimethylsilyl)diaminophosphine, 3232

DropBooks

PHOSPHORUS COMPOUNDS

Groups falling within this class are:

ALKYLHALOPHOSPHINES, ALKYLPHOSPHINES
tert-BUTYL PEROXOPHOSPHATE ESTERS
N-CHLORINATED PHOSPHORUS AMIDES
HALOPHOSPHINES, METAL PHOSPHINATES
METAL PHOSPHORUS TRISULFIDES
NON-METAL OXIDES, NON-METAL SULFIDES
PHOSPHINES, PHOSPHORUS ESTERS

PHOSPHORUS ESTERS $(RO)_3P$, $(RO)_3P{:}O$, $(RO)_2P(S)SR'$ etc.

1. Anon., *Loss Prev. Bull.*, 1979, (030), 159–160
2. *See entry* SELF-ACCELERATING REACTIONS
3. Lhomme, V. *et al., Ind. Eng. Chem., Prod. Res. Dev.*, 1984, **23**, 98–102

Two incidents involving thermal decomposition of an unspecified phosphorus ester insecticide which unintentionally became heated to 150–160°C are described. In one case the overheating arose from a relatively slow exotherm occurring at 90–100°C, and in the second, material at 55°C was heated instead of being cooled

[1]. A number of phosphate and thiophosphate esters are of limited thermal stability and undergo highly exothermic self-accelerating decomposition reactions which may be further catalysed by impurities. The potential hazards can be reduced by appropriate thermal control measures. An example is the substitution of hot water at 60°C for pressurised steam to melt a solid phosphate ester, which on adiabatic calorimetric examination was found to have a time to maximum decomposition rate of 6 h at 110° but 11 h at 100°C [2]. The combined use of vapour phase pyrolysis to decompose various phosphorus esters, and of GLC and mass spectrometry to analyse the pyrolysis products, allowed a thermal degradation scheme to be developed for phosphorus esters [3]. Individually indexed compounds are:

Allyl phosphorodichloridite, 1169
Bis(trimethylsilyl) phosphonite, 2611
O−*O*-*tert*-Butyl diphenyl monoperoxophosphate, 3712
O−*O*-*tert*-Butyl di(4-tolyl) monoperoxophosphate, 3763
Diallyl phosphite (Di-2-propenyl phosphonite), 2456
Dibenzyl phosphite, 3658
Dibenzyl phosphorochloridate, 3650
Di(*O*−*O*-*tert*-butyl) ethyl diperoxophosphate, 3374
Dibutyl hydrogen phosphite, 3086
Diethyl ethanephosphonite, 2572
Diethyl 4-nitrophenyl phosphate, 3329
Diethyl 4-nitrophenyl thionophosphate, 3328
Diethyl phosphite, 1733
∗ Diethyl phosphorochloridate, 1681
Dimethyl 2-chloro-4-nitrophenyl thionophosphate, 2960
Dimethyl 3-chloro-4-nitrophenyl thionophosphate, 2961
Dimethyl *N*,*N*-dichlorophosphoramidate, 0901
∗ 2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclooctane, 2548
Dimethyl ethanephosphonite, 1732
∗ Dimethyl hydrazidophosphate, 0959
O, *O*-Dimethyl *S*-methylcarbamoylmethyl phosphorodithioate, 2009
Dimethyl 4-nitrophenyl thionophosphate, 2979
Dimethyl phosphoramidate, 0952
∗ Diphenyl azidophosphate, 3489
∗ Potassium *O*,*O*-diphenyl dithiophosphate, 3481
∗ Pyrocatecholato(2−)(quinolin-8-olato-*N*,*O*)-trioxygenido(2−) phosphorus, 3678
Triallyl phosphate, 3184
Trimethyl phosphate, 1318
Trimethyl phosphite, 1315
Trimethyl thiophosphate, 1316

PHYTOSTEROLS **(several compounds and isomers)**

Dry and finely divided phytosterol materials are a significant dust explosion hazard.
See entry DUST EXPLOSION INCIDENTS (reference 22)

1. Anon., *Angew. Chem. (Nachr.)*, 1954, **2**, 21
2. Hopper, J. D., *J. Franklin Inst.*, 1938, **225**, 219–225
3. Kast, H., *Chem. Abs.*, 1911, **5**, 2178
4. Nakamura, K. *et al.*, *Bull. Chem. Soc. Japan*, 1987, **60**, 2037–2040

While the m.p. of a picrate was being determined in a silicone oil bath approaching 250°C, an explosion occurred, scattering hot oil. It is recommended that picrates, styphnates and similar derivatives should not be heated above 210°C in a liquid-containing m.p. apparatus [1]. In an investigation of the sensitivity to impact of a range of hydrated and anhydrous metal picrates, anhydrous nickel picrate was found to be particularly sensitive [2]. The explosive characteristics of a range of 13 mono- to tri-valent metal picrates and methylpicrates was determined [3]. The hydrated picrates of the lanthanide (rare-earth) metals were prepared from the carbonates. Dysprosium and ytterbium gave octahydrates, while lanthanum, cerium, praseodymium, neodymium, samarium, europium and gadolinium gave undecahydrates, all being stable to drying in air. Drying under vacuum, by desiccation, or by warming just above 30°C could, however, give the anhydrous picrates, of which the explosion temperatures were all above 300°C [4].

Individually indexed compounds are:

2,2,4-Trimethyldecahydroquinolinium picrate, 3765
Ammonium picrate, 2322
Calcium picrate, 3430
∗ Cobalt(II) picramate, 3460
Copper(II) picrate, 3432
Lanthanum picrate, 3741
Lead(II) picrate, 3436
Manganese picrate hydroxide, 3742
Mercury(II) picrate, 3433
S-7-Methylnonylthiouronium picrate, 3737
Nickel picrate, 3435
Potassium picrate, 2085
Sodium picrate, 2086
Zinc picrate, 3437

See also ARENECYCLOPENTADIENYLIRON(II) PICRATES

DropBooks

PLANT CLEANING INCIDENTS

1. Anon., *Loss Prev. Bull.*, 1980, (035), 7–11; 1981, (038), 23–27
2. Peischel, M., *Proc. 11th Int. Symp. Prev. Occup. Risks Chem. Ind.*, 721–731, Heidelberg, ISSA, 1987

The need to provide both detailed instructions and proper supervision for plant cleaning operations, either before maintenance operations in any plant, or between different product runs in multi-use batch plant, is stressed. Several examples are given of untoward reactions and incidents which occurred when either or both of the above requirements were lacking. The importance of checking the effectiveness

of cleaning operations before restarting plant was highlighted by further examples of incidents [1]. During cleaning of a 6 m^3 tank by pump-recycled solvent mixture, electrostatic sparks ignited the vapour–air mixture and blew off the tank lid [2].

Some individually indexed examples will be found under:
Nitric acid, 4436
Nitric acid, : Alcohols, 4436
Nitric acid, : Polyurethane foam, 4436
Nitric acid, : Resorcinol, 4436
Phosphoryl chloride, : Water, 4149
See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

PLATINUM COMPOUNDS

Cotton, F. A., *Chem. Rev.*, 1955, **55**, 577
Several platinum compounds, including trimethylplatinum derivatives, are explosively unstable. Some compounds of the other platinum group metals are also of limited stability. Individually indexed compounds are:
Amminedecahydroxydiplatinum
Amminepentahydroxyplatinum, 4571
Ammonium hexachloroplatinate, 4186
Ammonium tetranitroplatinate(II), 4578
Diacetatoplatinum(II) nitrate, 1510
Diamminedichloroaminotrichloroplatinum(IV), 4179
∗ Diamminedihydroxyosmium, 4572
∗ Diamminepalladium(II) nitrate, 4562
∗ Diamminepalladium(II) nitrite, 4559
cis-Diammineplatinum(II) nitrite, 4560
∗ Dodecamethyltetraplatinum(IV) azide, 3590
∗ Dodecamethyltetraplatinum(IV) perchlorate, 3587
Hexamethyldiplatinum, 2606
∗ Palladium(II) acetate, 1541
∗ Palladium(III) oxide, 4848
∗ Palladium(IV) oxide, 4835
∗ Perchloratotris(triethylphosphine)palladium(II) perchlorate, 3778
Platinum(IV) oxide, 4836
∗ Potassium dinitrooxalatoplatinate(2−), 0988
Potassium hexaazidoplatinate(IV), 4665
Potassium hexachloroplatinate, 4187
Sodium hexahydroxyplatinate(IV), 4564
Tetraamminehydroxynitratoplatinum(IV) nitrate, 4594
∗ Tetraamminepalladium(II) nitrate, 4588
Tetramethylplatinum, 1768
Tetraammineplatinum(II) nitrate, 4589
∗ *N,N,N′,N′*-Tetramethylethane-1,2-diamine, trimethylpalladium(IV) bromide, 3225

∗ *N,N,N′,N′*-Tetramethylethane-1,2-diamine,
trimethylpalladium(IV) iodide, 3226
Triamminenitratoplatinum(II) nitrate, 4582
Trimethylplatinum hydroxide, 1329

See also GOLD COMPOUNDS

See other HEAVY METAL DERIVATIVES

PLATINUM GROUP METALS

Ullmann, 1992, Vol. A21, 125/6

A section on explosion hazards is included in the monograph on platinum group metals. Most of the hazards are associated with their activity as redox catalysts and are already covered in this work. Warning is given of violent alloy formation with e.g. lithium and titanium, especially by platinum and ruthenium. Alloys, or compounds, with metalloids may also be formed energetically. Absorption and sudden release of hydrogen, which will then be ignited by the catalytic metal (itself pyrophoric if finely divided) is a frequent hazard, worst for ruthenium which can retain more hydrogen than the others. Compounds and complexes incorporating both oxidant anions and oxidisable ligands (ammonia, organic moieties etc.) are likely to prove shock sensitive explosives.

See AMMINEMETAL OXOSALTS, ORGANOMETALLIC NITRATES

POLY(AMINIUM) PERCHLORATES $[\text{-}(CH_2)_m N^+H_{2-}\text{-}]n\ nClO_4^-$

Thomas, T. J. *et al., Amer. Inst. Aero. Astron. J.*, 1976, **14**, 1334–1335

Ignition temperatures were determined by DTA for the perchlorate salts of ethylamine, isopropylamine, 4-ethylpyridine, poly(ethyleneimine), poly(propyleneimine), and poly(2- or 4-vinylpyridine). In contrast to the low ignition temperatures (175–200°C) of the polymeric salts, mixtures of the polymeric bases with ammonium perchlorate decompose only above 300°C.

See AMINIUM PERCHLORATES

See other PERCHLORATE SALTS OF NITROGENOUS BASES

POLYAZACAGED METAL PERCHLORATES

Harrowfield, J. MacB. *et al., Inorg. Synth.*, 1980, **20**, 85–86

A wide range of macrocyclic or multicyclic polynitrogen 'cage' ligands have been prepared in recent years and used to study the metal ion shielding and other effects of deep complexing of metal salts. In several cases it is known that the perchlorate salts of such complexes are highly unstable or explosive, and it must be assumed that this is a likely generality for the majority of such perchlorate salts. There are separate entries with specific warnings for the groups CLATHROCHELATED METAL PERCHLORATES, [14] DIENE-N_4 COMPLEXES, TETRAAZAMACROCYCLANEMETAL PERCHLORATES, AND TETRAMETHYL[14]TETRAENE-N_8 METAL PERCHLORATES but the 'Sepulchrate' metal complexes (of the reference above, prepared by the reaction

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sequence str04 p. S1-S7) of 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]-eicosane ('Bicyclo[6.6.6]ane-1,3,6,10,13,16,19,-N_8') are also likely to give unstable perchlorate salts.

CLATHROCHELATED METAL PERCHLORATES
[14] DIENE-N_4 COMPLEXES
TETRAAZAMACROCYCLANEMETAL PERCHLORATES
TETRAMETHYL[14]TETRAENE-N_8 METAL PERCHLORATES
AMMINEMETAL OXOSALTS

POLYCONDENSATION REACTION INCIDENTS

A number of runaway reaction incidents which have involved the formation of polymeric species differ from usual polymerisation reactions of monomers in that elimination reactions of various types have been involved. Individually indexed examples are:

2-Acetyl-3-methyl-4,5-dihydrothiophen-4-one
Benzyl alcohol, : Hydrogen bromide, Iron
Benzyl bromide, : Molecular sieve
Benzyl chloride, : Catalytic impurities
Benzyl fluoride
1,2-Bis(chloromethyl)benzene
Ethylene oxide, : Contaminants
Furoyl chloride
4-Methoxy-3-nitrobenzoyl chloride

See related POLYMERISATION INCIDENTS
See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

POLY(DIMERCURYIMMONIUM) COMPOUNDS $(Hg{=}N^{+}{=}HgZ^{-})_n$

1. Ciusa, W., *Chem. Abs.*, 1943, **37**, 3271.9; 1944, 38, 4133.4
2. Sorbe, 1968, 97
3. Bailar, 1973, Vol. 3, 313

Several explosive salts including the acetylide, azide, borate, bromate, chlorate, chromate, iodate (and ammonium iodate double salt), nitrite, perchlorate (and ammonium perchlorate double salt), periodate, permanganate, picrate and trinitrobenzoate were prepared. The 3 latter salts and the acetylide, azide and bromate are impact-sensitive detonators [1]. It appears probable that many of the explosively unstable compounds [2], formed in various ways from interaction of mercury or its compounds with ammonia or its salts, may have the common polymeric structure now recognised for Millon's base [3]. This is a silica-like network of N^{+} and Hg in 4- and 2-coordination, respectively, with OH^{-} and water in the interstitial spaces. Individually indexed compounds are:

Poly(dimercuryimmonium acetylide)
Poly(dimercuryimmonium azide)
Poly(dimercuryimmonium bromate)
Poly(dimercuryimmonium hydroxide)

Poly(dimercuryimmonium iodide hydrate)
Poly(dimercuryimmonium perchlorate)
Poly(dimercuryimmonium permanganate)
See other MERCURY COMPOUNDS, *N*-METAL DERIVATIVES

POLY(DIMETHYLSILYL)CHROMATE **$[Me_2SiOCrO_2O]_n$**

See Bis(trimethylsilyl) chromate

POLYMERIC PEROXYACIDS

1. Takagi, T. J., *Polymer Sci. (B), Polymer Lett.*, 1967, **5**, 1031–1035
2. Harrison, C. R. *et al., J. Chem. Soc., Chem. Comm.*, 1974, 1009
3. Oshike, Y. *et al., Chem. Abs.*, 1987, **107**, 59502

An ion exchange resin based on poly-acrylic or -methacrylic acids and containing aliphatic peroxyacid groups [1] readily explodes on impact, but a polystyrene resin containing aromatic peroxyacid groups on ~70% of the phenyl residues could not be caused to explode on impact [2]. Polymeric peroxides formed from sodium peroxide and the acid chlorides of dibasic acids show poor solubility in monomers and solvents and poor safety characteristics in handling. However, the polymeric peroxides formed from the acid chlorides derived from oligo-esters of adipic acid and ethylene glycol are better in these respects [3].

See 2,2′-Azobis(2-amidiniopropane) peroxodisulfate
See PEROXYACIDS

DropBooks

POLYMERISATION INCIDENTS

1. Anon., *CISHC Chem. Safety Summ.*, 1978, **49**(194), 32, 33
2. Schmidt, C. U. *et al., Chem. Eng. Sci.*, 1988, **43**, 2133–2137
3. King, 1991, 56
4. *Chemical Reaction Hazards,*, Barton, J. & Rogers, R., Rugby, IChE, 1993
5. Rowe, S. M., 1994, personal communication.
6. Frurip, D. J., *et al., Process Safety Progress*, 1995, **14**(2), 79
7. Editor's comments, 1998

In a first full scale attempt at a new polymerisation process, the thermally unstable initiator was charged and heated to reaction temperature, but there was then an unforeseen delay of an hour before monomer addition was started. The rate of polymerisation effected by the depleted initiator was lower than the addition rate of the monomer, and the concentration of the latter reached a level at which an uncontrollable polymerisation set in which eventually led to pressure-failure of the vessel seals. Precautions to prevent such occurrences are detailed. In another incident, operator error led to catalyst, condensing styrene and acrylonitrile being ducted into an unstirred weighing tank instead of a reactor. When the error was recognised, the reacting mixture was dropped into drums containing inhibitor. One of the sealed drums had insufficient inhibitor to stop the reaction, and it slowly heated and eventually burst [1]. The features and use of

a specially developed polymerisation reaction safety calorimeter to study critical polymerisation conditions are described [2]. Conditions and incidents for runaway polymerisation of a number of monomers are given [3]. Polymerisation has latterly overtaken nitration as the leading source of runaway reactions in the British chemical industry [4]. Runaway free-radical polymerisations can be suppressed by injection of a sub-percentage quantity of appropriate free radical traps, such as the anti-oxidants phenothiazine or butylcatechol. Note that this cannot be expected to inhibit condensation polymerisations, such as that of phenol and formaldehyde, which also are a common cause of accident [5]. Procedures for testing monomers for hazardous polymerisation potential have been devised [6].

Stabilisation of unsaturated monomers for storage is a complex phenomenon; acrylates, especially, are partially stabilised by atmospheric oxygen. The anti-oxidants added as stabilisers merely prevent the peroxides produced when oxygen terminates a radical chain from themselves subsequently acting as radical initiators. Acrylates stored with exclusion of air may polymerise violently even though stabilised. Since the core of a crystal will not hold any stabiliser, and probably no oxygen, melting solid monomers produces microdomains well set-up for polymerisation, which may warm the bulk to a temperature where thermal polymerisation becomes unstoppable. Melting frozen monomers, such as acrylamide or acrylic and methacrylic acids, has been a frequent cause of mishap [7].

Other polymerisation incidents are:

† Acrylaldehyde, 1145
Acrylamide, 1180
Acrylic acid, 1148
Acrylic acid, Initiator, Water, 1148
† Acrylonitrile, 1107
† Acrylonitrile, Initiators, 1107
† Acrylonitrile, Silver nitrate, 1107
† Acryloyl chloride, 1093
Allyl 4-toluenesulfonate, 3315
Aluminium chloride, Alkenes, 0062
3-Aminopropiononitrile
† Aziridine, Acids, 0863
2,2′-Azobis(2-amidiniopropane) chloride, 3089
† 1,3-Butadiene, 1480
† 1,3-Butadiyne, Arsenic pentafluoride, 1385
† 1-Buten-3-one, 1515
2-Buten-1-yl benzenesulfonate, 3316
† 2-Chloro-1,3-butadiene, 1451
† 1-Chloro-2,3-epoxypropane, Contaminants, 1162
2-Chloroethylamine, 0896
2-Chloroethylammonium chloride, Alkali, 0940
† Chloroethylene, 0730
Chloroperoxytrifluoromethane, Tetrafluoroethylene, 0319

Cyanamide, Water, 0404
2-Cyanoethanol, Acids, or Bases, 1181
Cyanogen fluoride, Hydrogen fluoride, 4294
† Cyclopentadiene, 1857
† Cyclopentadiene, : Potassium hydroxide, 1857
Diallyl phosphite, 2456
Diallyl sulfate, 2443
1,2-Di(3-buten-1-ynyl)cyclobutane, 3509
† 1,1-Dichloroethylene, 0695
1,4-Dicyano-2-butene, 2311
Diisocyanatomethane, Dimethylformamide, 1077
† Diketene, Acids, or Bases, or Sodium acetate, 1441
2,3-Epoxypropionaldehyde oxime, 1182
† Ethyl acrylate, 1913
† Ethylene oxide, 0829
† Formaldehyde, Phenol, 0416
6-Fulvenoselone, 2216
Furfuryl alcohol, 1880
Glycolonitrile, 0760
2,4-Hexadienal, 2383
† Hydrogen cyanide, 0380
4-Hydroxy-*trans*-cinnamic acid, 3136
N-Hydroxymethylacrylamide, 1571
Methacrylic acid, 1530
† Methyl acrylate, 1531
† 2-Methylaziridine, Acids, 1257
† Methyl methacrylate, Propionaldehyde, 1915
3-Methyl-2-penten-4-yn-1-ol, 2384
1-(1-Methyl-1-phenylethyl)-4-(2-propynyloxy)benzene, 3760
† Methyl vinyl ether, Acids, 1221
Nitrilotris(oxiranemethane), 3181
2-Nitropropene, 1183
Octakis(trifluorophosphine)dirhodium, Acetylenic esters, 4387
Phenylacetylene, 2912
† Propene, Lithium nitrate, Sulfur dioxide, 1198
† 2-Propen-1-ol, Sulfuric acid, 1223
Propiolaldehyde, 1085
† Propylene oxide, Sodium hydroxide, 4445
3-Propynethiol, 1152
3-Propynol, Mercury(II) sulfate, Sulfuric acid, Water, 4479
Styrene, Air, Polymerising styrene, 2945
Styrene, Butyllithium, 2945
Styrene, Dibenzoyl peroxide, 2945
Styrene, Initiators, 2945
† Tetrafluoroethylene, 0628
2,2,3,3-Tetrafluoropropanol, Potassium hydroxide, or Sodium, 1133

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Thiocyanogen, 1001
1,3,5-Triethynylbenzene, 3443
† Vinyl acetate, 1532
Vinylpyridine, 2759
See also VIOLENT POLYMERISATION
See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

POLYNITROALKYL COMPOUNDS **$C(NO_2)_n$, $O_2NC-CNO_2$**

1. Hammond, G. S. *et al., Tetrahedron*, 1963, **19** (Suppl. 1), 177, 188
2. Grakauskas, V. *et al., J. Org. Chem.*, 1978, **43**, 3485–3488

Trinitromethane ('nitroform'), dinitroacetonitrile, their salts and polynitroalkanes are all potentially dangerous, and must be carefully handled as explosive compounds [1]. Many congeners and derivatives of dinitromethane are explosive and require careful and appropriate handling [2]. Individually indexed compounds are:

N,N′-Bis(2,2,2-trinitroethyl)urea, 1875
∗ Borane–bis(2,2-dinitropropylhydrazine), 0137
Dichlorodinitromethane, 0328
∗ *N*-Dimethylethyl-3,3-dinitroazetidine, 2848
Dinitroacetonitrile, 0676
∗ 3,3-Dinitroazetidinium trifluoromethanesulfonate, 1495
1,1-Dinitro-3-butene, 1508
2,3-Dinitro-2-butene, 1509
Dinitrodiazomethane, 0545
5(1,1-Dinitroethyl)-2-methylpyridine, 2965
Dinitromethane, 0410
2,4-Dinitropentane isomers, 1953
2,2-Dinitropropylhydrazine, 1277
3(2,3-Epoxypropyloxy)2,2-dinitropropyl azide, 2403
2-Fluoro-2,2-dinitroethanol, 0750
Fluorodinitromethane, 0374
Fluorodinitromethyl azide, 0341
Fluorotrinitromethane, 0340
1,1,1,3,5,5,5-Heptanitropentane, 1854
Hexanitroethane, 1014
Lithium 1,1,2,2-tetranitroethanediide, 0994
Potassium dinitroacetamide, 0709
Potassium dinitromethanide, 0377
Potassium 1,1-dinitropropanide, 1175
Potassium 1,1,2,2-tetranitroethanediide, 0989
Potassium trinitromethanide, 0530
Silver cyanodinitromethanide, 0567
Silver dinitroacetamide, 0689
Silver trinitromethanide, 0302
Sodium dinitroacetamide, 0712

Sodium dinitromethanide, 0384
Sodium 5-(dinitromethyl)tetrazolide, 0681
Sodium 1,1,2,2-tetranitroethanediide, 1007
Sodium 2,2,2-trinitroethanide, 0713
Tetrakis(2,2,2-trinitroethyl) orthocarbonate, 3132
∗ 1,3,5,7-Tetranitroadamantane, 3310
Tetranitromethane, 0546
1,1,1-Triazidodinitroethane, 0683
Trinitroacetonitrile, 1009
1,1,1-Trinitroethane, 0775
2,2,2-Trinitroethanol, 0776
Trinitromethane, 0385
∗ 1,3,5-Tris(nitromethyl)benzene, 3145
Tris(2,2,2-trinitroethyl) orthoformate, 2786

See FLUORODINITROMETHYL COMPOUNDS, TRINITROETHYL ORTHOESTERS

POLYNITROARYL COMPOUNDS $Ar(NO_2)_n$

1. Urbanski, 1964, Vol. 1
2. Shipp, K. G. *et al., J. Org. Chem.*, 1972, **37**, 1966
3. Shipp, K. G. *et al.*, US Pat. 3 941 853, 1976
4. Zenor, S., *Thermochim. Acta*, 1979, **31**, 269–283
5. Zhang, H. *et al., Chem. Abs.*, 1988, **109**, 12825
6. Kondrikov, B. N. *et al., Chem. Abs.*, 1996, **125**, 172589

DropBooks

Polynitro derivatives of monocyclic aromatic systems (trinitrobenzene, trinitrotoluene, tetranitro-*N*-methylaniline, trinitrophenol, etc.) have long been used as explosives [1]. It has been found that a series of polynitroderivatives of biphenyl, diphenylmethane and 1,2-diphenylethylene (stilbene) are explosives liable to detonate on grinding or impact [2]. The same may be true of other polynitro derivatives of polycyclic systems not normally used as explosives (e.g. polynitro-fluorenones, -carbazoles, etc. Penta- and hexa-nitrobenzophenones are also high-energy explosives [3]. The thermal stability of 33 polynitroaromatics was studied by DTA [4]. Two empirical equations relating the heat of decomposition to the heat of detonation have been developed and used to calculate the heats of detonation for 47 polynitroaryl compounds [5].

The presence of 2 or more nitro groups (each with 2 oxygen atoms) on an aromatic nucleus often increases the reactivity of other substituents and the tendency towards explosive instability as oxygen balance is approached.

The effect of sulphuric acid, a likely impurity from the usual preparation, in increasing sensitivity to detonation and decomposition has been studied [6].

Bases, or Salts

Uhlmann, P. W., *Chem. Ztg.*, 1914, **38**, 389–390

In view of previous violent or explosive reactions, heating of di- and tri-nitroaryl compounds with alkalies, ammonia or *O* -ethylsulfuric acid salts in autoclaves should be avoided.

See Diethyl sulfate: 3,8-Dinitro-6-phenylphenanthridine
See also NITROAROMATIC–ALKALI HAZARDS

Potassium

Batz, M. L. *et al., J. Org. Chem.*, 1997, **62**, 2045

Potassium salts of the radical anions $\cdot N^{+}$ $(O^{-})_2Ar$ were prepared by treating nitroaromatics (nitrobenzene, o-, m-, & p-dinitrotoluene, 2,4,6-trinitrotoluene and trinitrobenzene with potassium in liquid ammonia and allowing the ammonia to evaporate. All were exceedingly sensitive, exploding on mild agitation of the flask onto which they had been deposited. They decomposed non-explosively in solution to give potassium nitrite and polymers (explosive in the case of TNT) Hydrogen cyanide was among the explosion products of those bearing ortho methyl groups. Presumably other alkali metals would form similar compounds.

Individually indexed compounds are:

2-Acetylamino-3,5-dinitrothiophene, 2280
2-Amino-4,6-dinitrophenol, 2278
3-Amino-2,5-dinitrotoluene, 2783
Ammonium 3-methyl-2,4,6-trinitrophenoxide, 2803
Ammonium picrate, 2322
∗ Ammonium 2,4,5-trinitroimidazolide, 1144
2-Azido-3,5-dinitrofuran, 1384
2,2′-Azo-3,5-dinitropyridine, 3238
2-Benzylideneamino-4,6-dinitrophenol, 3600
Bis(2,4-dinitrophenyl) disulfide, 3449
Bis(2-nitrophenyl) disulfide, 3465
1,2-Bis(2-nitrophenyl)ethane, 3646
6-Bromo-2,4-dinitrobenzenediazonium hydrogen sulfate, 2097
5-*tert* -Butyl-2,4,6-trinitro-1,3-xylene, 3532
Calcium picrate, 3430
2-Chloro-4,6-dinitroaniline, 2153
4-Chloro-2,6-dinitroaniline, 2154
1-Chloro-2,4-dinitrobenzene, 2098
6-Chloro-2,4-dinitrobenzenediazonium hydrogen sulfate, 2102
2-Chloro-1,3-dinitro-5-trifluoromethylbenzene, 2637
∗ Cobalt(II) picramate, 3460
Copper(II) 3,5-dinitroanthranilate, 3627
Copper(II) picrate, 3432
1,5-Dichloro-2,4-dinitrobenzene, 2077
1,5-Difluoro-2,4-dinitrobenzene, 2080
1,8-Dihydroxy-2,4,5,7-tetranitroanthraquinone, 3621
mixo-Dimethoxydinitroanthraquinone, 3701
2,4-Dinitroaniline, 2277
1,2-Dinitrobenzene, 2194
1,3-Dinitrobenzene, 2195
1,4-Dinitrobenzene, 2196

1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3702
2,4-Dinitrobenzenediazonium hydrogen sulfate, 2206
4,6-Dinitro-1,3-benzenediol, 2198
∗ 2,4-Dinitrobenzenesulfenyl chloride, 2099
2,4-Dinitrobenzenesulfonyl chloride, 2100
4,6-Dinitrobenzofurazan *N*-oxide, 2089
2,6-Dinitrobenzyl bromide, 2672
4,6-Dinitro-2-*sec*-butylphenol, 3306
∗ 5,6-Dinitro-2-dimethylaminopyrimidinone, 2358
3,5-Dinitro-4-hydroxybenzenediazonium 2-oxide, 2090
3,5-Dinitro-2-methylbenzenediazonium-4-oxide, 2666
3,5-Dinitro-6-methylbenzenediazonium-2-oxide, 2667
2,5-Dinitro-3-methylbenzoic acid, 2919
1,5-Dinitronaphthalene, 3242
2,6-Dinitro-4-perchlorylphenol, 2101
2,4-Dinitrophenol, 2197
2,4-Dinitrophenylhydrazinium perchlorate, 2351
O-(2,4-Dinitrophenyl)hydroxylamine, 2279
3,8-Dinitro-6-phenylphenanthridine, 3780
4,6- or 5,6- or 5,7-Dinitro-1-picrylbenzotriazoles, 3439
3,5-Dinitro-2-toluamide, 2941
2,4-Dinitrotoluene, 2726
2,3-Epoxypropionaldehyde 2,4-dinitrophenylhydrazone, 3130
∗ 1-Fluoro-2,4-dinitrobenzene, 2108
2-Formylamino-3,5-dinitrothiophene, 1823
Hexanitrobenzene, 2632
4-Hydroxy-3,5-dinitrobenzenearsonic acid, 2220
2-Hydroxy-3,5-dinitropyridine, 1822
2-Iodo-3,5-dinitrobiphenyl, 3450
Lead 2-amino-4,6-dinitrophenoxide, 3469
Lead(II) picrate, 3436
Lead 2,4,6-trinitroresorcinoxide, 2071
Manganese picrate hydroxide, 3742
Mercury(II) picrate, 3433
∗ 2-(1-Methylheptyl)-4,6-dinitrophenyl crotonate, 3764
3-Methyl-2,4,6-trinitrophenol, 2703
Nickel 2,4-dinitrophenoxide hydroxide, 3745
Nickel picrate, 3435
1-Nitro-3-(2,4-dinitrophenyl)urea, 2705
5-Nitro-2-picryltetrazole, 2638
4-Nitro-1-picryl-1,2,3-triazole, 2886
Pentanitroaniline, 2093
Picric acid (2,4,6-Trinitrophenol), 2118
Picryl azide, 2092
1-Picryl-1,2,3-triazole, 2893
Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide, 2256

DropBooks

Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide, 2114
Potassium 4-methoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienonide, 2722
Potassium 6-*aci*-nitro-2,4-dinitro-2,4-cyclohexadieniminide, 2113
Silver 2-azido-4,6-dinitrophenoxide, 2075
Silver 3,5-dinitroanthranilate, 2642
Silver hexanitrodiphenylamide, 3429
Sodium 4,4-dimethoxy-1-*aci*-nitro-3,5-dinitro-2,5-cyclohexadienide, 2951
Sodium 2,4-dinitrophenoxide, 2115
Sodium 2-hydroxymercurio-6-nitro-4-*aci*-nitro-2,5-cyclohexadienonide, 2111
Sodium 6-*aci*-nitro-4-nitro-2,4-cyclohexadieniminide, 2200
2,3,4,6-Tetranitroaniline, 2122
N,2,3,5-Tetranitroaniline, 2121
N,2,4,6-Tetranitroaniline, 2123
1,3,6,8-Tetranitrocarbazole, 3442
N,2,4,6-Tetranitro-*N*-methylaniline, 2706
1,3,6,8-Tetranitronaphthalene, 3237
2,3,4,6-Tetranitrophenol, 2091
2,4,6-Tri(2-acetylhydrazino)-1,3,5-trinitrobenzene, 3535
1,3,5-Triaminotrinitrobenzene, 2324
1,3,5-Trifluorotrinitrobenzene, 2057
2,4,6-Trinitrobenzoic acid, 2640
Trinitrophloroglucinol, 2120
Trinitroresorcinol, 2119
2,4,5-Trinitrotoluene, 2702
2,4,6-Trinitrotoluene, 2701
∗ 1,3,5-Tris(nitromethyl)benzene, 3145
Zinc picrate, 3437

See also NITROARYL COMPOUNDS

POLYNITROAZOPYRIDINES $(O_2N)_2C_5H_2NN{=}NNC_5H_2(NO_2)_2$

Coburn, M. D., *J. Heterocyclic Chem.*, 1974, **11**, 1099–1100

Most of a series of azodinitropyridines and their hydrazine precursors were explosive, with a sensitivity comparable to that of RDX. Individual compounds are:
2,2′-Azo-3,5-dinitropyridine, 3238
2,6-Bis(2-picrylhydrazino)-3,5-dinitropyridine, 3735
2,6-Bis(picrylazo)-3,5-dinitropyridine, 3734
3,5-Dinitro-2-(picrylazo)pyridine, 3387
1-(3,5-Dinitro-2-pyridyl)-2-picrylhydrazine, 3389

See other HIGH-NITROGEN COMPOUNDS, POLYNITROARYL COMPOUNDS

POLYPEROXIDES

This group covers polymeric peroxides of indeterminate structure rather than polyfunctional macromolecules of known structure. These usually arise from autoxidation of susceptible monomers and are of very limited stability or

explosive. Polymeric peroxide species described as hazardous include those derived from butadiene (highly explosive); isoprene, dimethylbutadiene (both strongly explosive); 1,5-*p*-menthadiene, 1,3-cyclohexadiene (both explode at 110°C); methyl methacrylate, vinyl acetate, styrene (all explode above 40°C); diethyl ether (extremely explosive even below 100°C); and 1,1-diphenylethylene, cyclopentadiene (both explode on heating).

Individually indexed entries are:
† Chloroethylene, 0730
† 1,3-Cyclohexadiene, 2361
† Cyclopentadiene, : Oxygen, 1857
† 1,1-Dichloroethylene, 0695
† Diethyl ether, 1697
2,4-Diethynyl-5-methylphenol, 3393
2,4-Diethynylphenol, 3244
2,3-Dimethyl-1,3-butadiene, 2407
6,6-Dimethylfulvene, 2967
1,1-Diphenylethylene, : Oxygen, 3642
Formaldehyde oxide polymer, 0419
† 1,5-Hexadien-3-yne, 2291
Hydrogen peroxide, : Poly(hydroxyacrylic acid lactone), etc., 4477
1,5-*p*-Menthadiene, 3338
2-Methylacryaldehyde oxime, 1568
† Methyl methacrylate, 1915
Oxygen (Gas), : Cyclooctatetraene, 4831
Oxygen (Gas), : Tetrafluoroethylene, 4831
Poly(1,3-butadiene peroxide), 1533
Poly(1,3-cyclohexadiene peroxide), 2386
Poly(dimethylketene peroxide), 1536
Poly(ethylidene peroxide), 0835
∗ Poly(peroxyisobutyrolactone), 1536
Poly(styrene peroxide), 2957
Poly(vinyl acetate peroxide), 1539
Styrene, : Oxygen, 2945
† Tetrafluoroethylene, 0628
† Vinyl acetate, 1532
See Hydrogen peroxide: Ketones, Nitric acid

PrepBooks

POLYPROPYLENE POWDER

Anon., *CISHC Chem. Safety Summ.*, 1979, **50**, 91
Polypropylene powder was being conveyed by suction through a duct system as an air dispersion, fines being retained in a filter trap upstream of the centrifugal fans. However, the relatively coarse filter allowed very fine powder to pass and it was eventually retained over a long period of time in a silencer on the fan outlet. The thickening deposit eventually self-heated and ignited, and the fire spread very

rapidly in the air-stream. A second fire, also apparently with polypropylene powder, occurred in a flash-dryer and cyclone system. Washing of the dryer case with water had led to build-up of aggregated powder which had degraded, melted and ignited. Nitrogen purging has been introduced as a preventive measure.
See other SELF-HEATING AND IGNITION INCIDENTS

PRECIOUS METAL DERIVATIVES

Hasenpusch, W., *Chem.-Ztg.*, 1987, **111**(2), 57–60
In a review of explosions involving derivatives of gold, silver and platinum, reactions of ammonia with gold and silver compounds, and of hydrogen in presence of platinum compounds are emphasised.
See also FULMINATING METALS, HEAVY METAL DERIVATIVES, HYDROGENATION CATALYSTS, HYDROGENATION INCIDENTS

PREPARATIVE HAZARDS

Preparative hazards have been noted for the following compounds:
4-Acetoxy-3-methoxy-2-nitrobenzaldehyde, 3266
Acetyl chloride, 0735
Aluminium copper(I) sulfide, 0084
3-Amino-2,5-dinitrotoluene, 2783
2-Amino-5-nitrothiazole, 1117
6-Aminopenicillanic acid *S*-oxide, 3010
4-Amino-4*H*-1,2,4-triazole, 0812
Azidosilane, 4501
Aziridine, 0863
1,1′-Azo-[2-methyl-1,2-dicarbadecaborane(14)], 2624
2-Azoxyanisole, 3653
1,4-Benzenediol–oxygen complex, 2334
Benzeneperoxysulfonic acid, 2341
Benzeneseleninic acid, 2335
Benzeneseleninic anhydride, 3495
Benzenethiol, 2344
2,2′-Bi-1,3-dithiole, 2215
2,2′-Bipyridyl 1-oxide, 3258
Bis(cyclopentadienyl)lead, 3294
Bis-*N*(imidosulfurdifluoridato)mercury, 4342
Bismuth trisulfide, 0234
1,2-Bis(2-nitrophenyl)ethane, 3646
1,3-Bis(trifluoromethyl)-5-nitrobenzene, 2885
Bis(trifluoromethyl)sulfur difluoride, 0648
4-Bromocyclopentene, 1884
Bromoethane, 0846
Bromogermane, 0246
4-Bromomethylbenzoic acid, 2926

2-Bromo-4-methylpyridine *N*-oxide, 2297
3-Bromopyridine, 1827
3-Bromo-1,1,1-trichloropropane, 1126
Butylbenzene, 3323
tert-Butyl hydroperoxide, 4477
N-*tert*-Butylphthalisoimidium tetrafluoroborate, 3521
Butylsodium, 1667
Cadmium selenide, 3959
4-Chloro-2,6-dinitroaniline, 2154
3-Chloro-1,3-diphenylcyclopropene, 3679
2-Chloro-5-methylaniline, 2793
2-Chloro-5-nitrobenzenesulfonic acid, 2144
Chloronitromethane, 0396
3-(4-Chlorophenyl)butanoic acid, 3297
2-(4-Chlorophenyl)-1,1-dimethylethyl hydroperoxide, 3018
4-Chlorophenyl isocyanate, 2648
Chlorotetrafluorophosphorane, 3987
Chlorotrimethylsilane, 1304
Chromyl acetate, 1494
Chromyl azide, 4239
Cyanocyclopropane, 1463
Cyanogen chloride, 0323
4-Cyano-3-nitrotoluene, 2917
cis-Cyclododecene, 3351
1,2-Cyclohexanedione, 2385
Decafluoro-2,5-diazahexane 2,5-dioxyl, 1372
2-Deuterobicyclo[2.2.1]hept-2-ene, 2811
Diacetatoplatinum(II) nitrate, 1510
Diallyl ether, 2431
2,3-Diazabicyclo[2.2.2]octa-2,5-diene *N*-oxide, 2374
2,4-Diazido-6-dimethylamino-1,3,5-triazine, 1876
1,2-Diazido-1-phenylethane, 2954
Diazomethyldimethylarsine, 1240
1,5-Dibenzoylnaphthalene, 3845
Diborane(6), 0166
Dibromogermane, 0267
Di-*tert*-butyl peroxide, 3074
2,4-Di-*tert*-butyl-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine, 3377
3,4-Dichloroaniline, 2241
cis-Dichlorobis(2,2′-bipyridyl)cobalt(III) chloride, 3799
Dichloromaleimide, 1378
N,N-Dichloropentafluorosulfanylamine, 4060
4-(2,4-Dichlorophenoxy)butyric acid, 3272
trans-Dichlorotetrapyridinecobalt(III) chloride, 3802
Diethylaminosulfinyl chloride, 1679

DropBooks

Diethyl 4-nitrophenyl phosphate, 3329
Diethyl trifluoroacetosuccinate, 3320
1,4-Diethynylbenzene, 3241
1,5-Difluoro-2,4-dinitrobenzene, 2080
Difluorotrifluoromethylphosphine oxide, 0360
4-Dimethylaminoacetophenone, 3321
2-(Dimethylaminomethyl)fluoroferrocene, 3612
3,5-Dimethylbenzoic acid, 3152
3,5-Dimethyl-4-[*I,I*-bis(trifluoroacetoxy)iodo]isoxazole, 3115
3,3-Dimethyl-1-butyne, 2408
Dimethyl *N,N*-dichlorophosphoramidate, 0901
Di-μ-methylenebis(methylpentamethylcyclopentadienyl)dirhodium, 3855
3,5-Dimethyl-3-hexyl hydroperoxide, 3075
3,7-Dimethyl-2,6-octadienal, 3346
Dimethylphenylphosphine oxide, 3002
2,2-Dimethylpropane, 1999
2,5-Dimethylpyrazine 1,4-dioxide, 2378
2,4-Dinitroaniline, 2277
3,5-Dinitrobenzenediazonium 2-oxide, 2087
4,6-Dinitro-1,3-benzenediol, 2198
2,4-Dinitrobenzenesulfonyl chloride, 2100
Dinitrogen oxide, 4744
7,8-Dioxabicyclo[4.2.2]-2,4,7-decatriene, 2955
Diperoxyazelaic acid, 3189
Diphenylamine, 3504
Dipyridinium dichromate, 3304
Disodium 4-nitrophenylphosphate, 2185
Dodecamethyltetraplatinum(IV) perchlorate, 3587
Ethanedial, 0723
Ethyl cyanoacetate, 1889
Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate, 2359
Ethyl iminioformate chloride, 1273
Ethylphenylthallium(III) acetate perchlorate, 3302
Fluorobis(trifluoromethyl)phosphine oxide, 0645
Fluorodiiodomethane, 0373
5-Fluoro-2-nitrophenol, 2167
Fluorotrinitromethane, 0340
Furoyl chloride, 1818
Hexacarbonyltungsten, 2636
1,4,7,10,13,16-Hexaoxacyclooctadecane, 3561
Hydrogen bromide, 0247
Hydrogen chloride, 3993
trans-4-Hydroperoxy-5-hydroxy-4-methylimidazolin-2-one, 1598
Hydroxyacetone, 1231
2-Hydroxy-2-methylglutaric acid, 2445
Indium bromide, 0289

Iodoethane, 0858
Iron(II) perchlorate, 4062
Isophthaloyl chloride, 2888
Magnesium, 4690
Mercury peroxide, 4606
4-Methoxybenzaldehyde, 2956
2-Methoxy-5-nitroaniline, 2802
4-Methoxy-3-nitrobenzoyl chloride, 2916
Methylborylene, 0425
Methyl iminioformate chloride, 0897
2-Methyl-5-nitrobenzenesulfonic acid, 2772
3-Methyl-4-nitropyridine *N*-oxide, 2317
Methylnitrothiophene, 1850
N-(3-Methylphenyl)-2-nitrobenzimidyl chloride, 3641
Methyltrifluoromethyltrichlorophosphorane, 0742
Molybdenum hexamethoxide, 2596
2-Nitroaniline, 2313
tert-Nitrobutane, 1660
Nitromesitylene, 3158
3-Nitrophthalic acid, 2906
3-Nitropropiophenone, 3141
N-Nitroso-6-hexanelactam, 2424
Nitrosylsulfuric acid, 4438
Nitroterephthalic acid, 2907
1,4-Octadecanolactone, 3773
1,4,8,11,15,18,22,25-Octamethyl-29*H*,31*H*-tetrabenzo[*b.g.l.q*]porphinato(2−)
cobalt(II), 3910
Osmium(IV) oxide, 4833
4-Oximino-4,5,6,7-tetrahydrobenzofurazan *N*-oxide, 2357
Pentaamminedinitrogenruthenium(II) salts, 4596
Pentafluoroorthoselenic acid, 4354
Pentanesulfonic acid, 2020
Perfluoro-*tert*-butanol, 1380
Peroxomonophosphoric acid, 4506
2-Phenyl-1,1-dimethylethyl hydroperoxide, 3332
N-Phenylhydroxylamine, 2356
Phenyllithium, 2259
Phenylsodium, 2287
Phosphoryl dichloride isocyanate, 0327
Phthalic anhydride, 2899
2-Piperidone, 1934
Platinum diarsenide, 0107
Poly(butadiyne), 1386
Poly(carbon monofluoride), 0337
Poly(ethylene terephthalate), 3262
Poly(selenium nitride), 4730

DropBooks

Potassium dithioformate, 0378
Potassium hexafluoromanganate(IV), 4363
Propionyl chloride, 2542
2,5-Pyridinedicarboxylic acid, 2696
Rhenium chloride trioxide, 4045
Rhenium hexamethoxide, 2603
Rhenium nitride tetrafluoride, 4344
Selenium dioxide, 4838
Silver tetrafluoroborate, 0005
Sodium 1,3-dichloro-1,3,5-triazine-2,4-dione-6-oxide, 3924
Sodium dihydrobis(2-methoxyethoxy)aluminate, 2575
Sodium hyponitrite, 4736
Sulfur dioxide, 4837
Sulfuryl azide chloride, 4031
Tantalum(IV) sulfide, 4903
Terephthalic acid, 2924
Tetraethylammonium periodate, 3090
Tetrafluorooxathietane-2,2-dioxide, 0635
Tetrafluorooxirane, 0632
Tetraiododiphosphane, 4637
5,10,15,20-Tetrakis(2-nitrophenyl)porphine, 3907
Tetramethoxyethylene, 2516
Tetramethylammonium ozonate, 1753
Tetramethyldiphosphane disulfide, 1766
Tetramethylsuccinodinitrile, 3007
7,7,10,10-Tetramethyl-1,2,5,6-tetroxecane-3,4-dione, 3349
Tetraphosphorus hexaoxide tetrasulfide, 4869
3-Thietanol-1,1-dioxide, 1238
3-Thiocresol, 2809
Titanium diiodide, 4630
Titanium tetraiodide, 4638
Triacetyl borate, 2390
2,4,6-Triallyloxy-1,3,5-triazine, 3530
2-(Tricarbonylferra)hexaborane(10), 1297
2,4,5-Trichlorophenol, 2107
Trifluoromethyl perchlorate, 0321
Trifluoromethylsulfur trifluoride, 0363
Trimethyl orthoformate, 1708
Trimethylsulfonium chloride, 1303
2,4,6-Trinitrobenzoic acid, 2640
Triphenylphosphine, 3756
1,1,1-Tris(aminomethyl)ethane, 2044
1,1,1-Tris(bromomethyl)methane, 1550
Tris(cyclopentadienyl)cerium, 3683
Tris(hydroxymethyl)methylamine, 1731
Tungsten hexamethoxide, 2604

Tungsten tetrabromide oxide, 0294
Undecaamminetetraruthenium dodecaoxide, 4598
Xenon difluoride dioxide, 4322
Xenon tetrafluoride oxide, 4346
Zinc ethylsulfinate, 1711
See 1,2-DIOLS, 1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE SALTS

PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

1. Grewer, T. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 657–664, Basle, SSCI, 1980
2. Klais, O. *et al., Proc. 4th Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, C24–C34, Rugby, IChE, 1983
3. Grewer, T. *et al., Hazards from Pressure*, IChE Symp. Ser. No. 102, 1–9, Oxford, Pergamon, 1987
4. Watanabe, N. *et al., Chem. Abs.*, 1988, **108**, 207227

Equipment was developed to measure the maximum pressure and rate of pressure increase during exothermic decomposition, and the results serve as useful criteria to assess hazards. For each of the 6 compounds examined at a vessel loading of 0.1–0.2 g/cm^3, the starting temperature, max. pressure (bar) and max. rate of rise (bar/s), respectively, are given below.

Azobenzene, 340/13/6.5; azoformamide, 260/194/925; diketene, 125/140/–; 4-nitroisopropylbenzene, 250/>182/830; 4-nitrophenol, 280/>199/1,030; 4-nitrosophenol, 120/23/5. It is concluded that the first and last compounds are of relatively low hazard [1]. Improved equipment has provided more accurate and detailed results for a further 7 compounds and has shown the effect of variations in the initial stage of decomposition on the final pressure attained, and of the increase in pressure causing a reduction in the rate of pressure rise. At 0.2 g/cm^3 loadings, comparable results are:-

A diazonium salt, 112/200/66; azoisobutyronitrile, 80/130/8,800; 1,3-diphenyltriazene, 140/95/420; 2-nitrobenzaldehyde, 200/945/8,700; 3-nitrobenzaldehyde, 190/830/4,100, 4-nitrobenzaldehyde, 200/960/4,700. Solids which deflagrate give substantially higher rates of pressure rise because the rate of pressure rise is not depressed by increase in pressure, e.g. ammonium dichromate, 227/510/68,000 [2].

Deflagration (progressive exothermic decomposition/combustion) may be rapid, as in propellant explosive compositions, or slow in non-explosive compounds. The high probability of deflagration in this latter type of industrially important materials, as indicated by the number of incidents involving the relatively few deflagrable non-explosives, has led to an investigation of deflagration and the pressure effects which accompany it. Deflagration rates (cm/min) measured by igniting the top of the material in a 5 cm diameter beaker and timing the downward progress were:- ammonium dichromate, 2.2; 1,3-diphenyltriazene, 2.0; hydroxylaminium sulfate, 5.6; 1-nitroso-2-naphthol, 0.74; 1-(2,4-dinitrophenylazo)-2-naphthol, 1.8; 4-nitrosophenol, 8; sodium 3-nitrobenzenesulfonate, 4.5 cm/min.

DropBooks

Most mononitroaryl compounds do not deflagrate, but mixed with an excess of sodium or potassium hydroxide they deflagrate readily. Some rates (cm/min) for such mixtures are:- 4-chloronitrobenzene + KOH (1:1.5 mol), 1.3; 4-nitrobenzoic acid + KOH (1:2 mol), 5.1; 4-nitrophenol + KOH (1:1.5 mol), 30; 2-nitrobenzaldehyde + active carbon (1.5:1 mol), 1.25 cm/min.

Pressure effects measured during deflagration with top-surface ignition in an unheated 200 ml autoclave, or during homogeneous decomposition (no ignition coil, autoclave heated slowly in an oven) led to some problems in interpreting the pressure-time curves in the latter case. Deflagration of 1,3-diphenyltriazene and of hydroxylaminium sulfate showed relatively slow rise of pressure (to 111, 250 bar in 600, 380 ms, respectively), while the results from homogeneous decomposition showed wider variations in the rate of pressure rise. Thus, 1,3-diphenyltriazene and 2-nitrobenzaldehyde showed slow rates of rise (to 132, 940 bar, in 600, 280 ms), while azoisobutyronitrile and ammonium dichromate showed fast rates (to 130, 480 bar during 30, 24 ms, respectively). Log-log plots of deflagration rates of pressure rise vs pressure show that for 1,3-diphenyltriazene, hydroxylaminium sulfate and 1-nitroso-2-naphthol, the rate is approximately proportional to pressure, while for ammonium dichromate it appears proportional to the square of the pressure [3].

In a study of deflagration of inorganic peroxide–combustible mixtures at compositions giving zero oxygen balance (and maximum rates of pressure rise), inorganic peroxides with cellulose give higher rates of rise than peroxoacids or hydrogen peroxide adducts (‘sodium percarbonate’), and some of these latter mixtures did not ignite. Mixtures of potassium chlorate with cellulose show high deflagration hazards and exhibit remarkable pressure increase effects [4].

Some incidents of this type may be found under:

Ammonium dichromate, 4246
Azoformamide, 0816
Azoisobutyronitrile, 3011
Azoisobutyronitrile, 3011
† *tert*-Butyl peroxybenzoate, 3401
4-Chloronitrobenzene, 2142
† 1,1-Difluoroethylene, 0700
† Diketene, 1441
1-(2,4-Dinitrobenzeneazo)-2-hydroxynaphthalene, 3702
1,3-Diphenyltriazene, 3506
1,3-Diphenyltriazene, 3506
† Ethylene oxide, : Sucroglyceride, 0829
Hydroxylaminium sulfate, 4575
3-Methyl-4-nitrophenol, 2766
2-Nitrobenzaldehyde, 2686
2-Nitrobenzaldehyde, 2686
4-Nitrobenzaldehyde, 2688
4-Nitrobenzoic acid, : Potassium hydroxide, 2695
4-Nitroisopropylbenzene, 3157

4-Nitrophenol, 2267
4-Nitrophenol, : Potassium hydroxide, 2267
1-Nitroso-2-naphthol, 3250
4-Nitrosophenol, 2264
Sodium 3-nitrobenzenesulfonate, 2184

See ISOXAZOLES
NITROBENZALDEHYDES
NITROBENZYL COMPOUNDS
PRESSURE RELIEF
ZINC BACITRACIN

PRESSURE RELIEF

1. Huff, J. E., *Proc. Int. Symp. Prev. Major Chem. Accid.*, Washington, 1987, 4.43–4.67, New York, AIChE, 1987
2. Burgoyne, J. H., *Hazards from Pressure*, IChE Symp. Ser. No. 102, 201–213, Oxford, Pergamon, 1987
3. Tippet, J. R. *et al.*, *ibid.*, 358–361
4. Fauske, H. K., *ibid.*, 133–141
5. Bettis, R. J. *et al.*, *ibid.*, 247–263
6. Fauske, H. K., *Plant/Oper. Progr.*, 1988, **7**(7), 3

The important role played by pressure relief arrangements to mitigate the effects of runaway exothermic reactions and to prevent catastrophic vessel failure is discussed. For full effectiveness, the pressure relief system must be included in the overall process design, and must be adequately sized to permit discharge of vessel contents at a safe pressure and to a safe location. Methods of achieving these objectives are presented [1], and problems associated with subsequent treatment of the materials from accidental discharges are discussed [2]. Methods of assessing relief requirements for reactive and non-reactive systems are considered, including runaway liquid phase reactions and fire-exposed liquid-filled storage vessels [4]. Special consideration is given to emergency releases involving 2-phase flow [4,5]. The scope of the AIChE design package of the Design Institute for Emergency Relief Systems (DIERS) has been extended to deal with both reactive and non-reactive mixtures being vented [6].

See PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

PROTEINS

1. Pitts, J. E., *Nature*, 1992, **360**, 94

It is suggested that crystalline proteins are explosive, as evidenced by the easily induced shattering of the microcrystals currently available [1]. Except, possibly, where mercuric nitrate is involved, the editor suspects this of being implosive collapse of a metastable ordering of molecules.

See ORGANOMETALLIC NITRATES

DrugBooks

PROPELLANTS

1. Gould, R. F., *Advanced Propellant Chemistry (ACS Monograph 54)*, Washington, Amer. Chem. Soc., 1966
2. Ullmann, 1993, *A22*, 185

Like other high energy materials deliberately made so (explosives and pyrotechnics) propellants in their proper use do not fall within the scope of this handbook. It is a field of considerable current development [2].

The above book [1] deals, in 26 chapters in 5 sections, with theoretical and practical aspects of the use and safe handling of powerful oxidants and their complementary reactive fuels. Materials include: nitrogen pentaoxide, perfluoroammonium ion and salts, nitronium tetrafluoroborate, hydrazinium mono- and diperchlorates, nitronium perchlorate, tricyanomethyl compounds, difluoramine and its alkyl derivatives, oxygen difluoride, chlorine trifluoride, dinitrogen tetraoxide, bromine trifluoride nitrogen fluorides, and liquid ozone–fluorine system.

See also ROCKET PROPELLANTS

PYRAZOLONE DYESTUFF PREPARATION

Anon., *Loss Prev. Bull.*, 1979, (030), 160

A 300 g sample of the monoazo product of coupling a diazotised nitroaminophenol onto a pyrazolone exploded violently during vacuum drying at 110°C. Small samples filtered at pH 7.5 had been dried uneventfully, but the large batch had been at pH 8.8 (so may have contained some diazophenoxide, formed as in reaction sequence str05, p. S1-S7). It was further found that parts of the oven were hotter by 20–30°C than the indicated temperature.

See ARENEDIAZONIUM OXIDES

PYROPHORIC ALLOYS

1. Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 163–164
2. Kirk-Othmer, 1982, Vol. 19, 494

Alloys of reactive metals are often more pyrophoric than the parent metals. Examples are alloys of titanium with zirconium; thorium with copper, silver or gold; uranium with tin, lead or gold; magnesium with aluminium; hafnium with iron [1]. Cerium amalgams and thorium–silver alloys are spontaneously flammable when dry [2]. Individually indexed alloys are:

Aluminium–lanthanum–nickel alloy
Cerium: Alone, or Metals, 3961
Lead–zirconium alloys, 4884
Silver–thorium alloy, 0004
Zinc amalgam, 4601

See other PYROPHORIC MATERIALS

PYROPHORIC CATALYSTS

1. *Laboratory Handling of Metal Catalysts*, in *Chem. Safety*, 1949, (2), 5
2. *Catalyst Handbook*, 180–181, London, Wolfe, 1970

A proposed Code of Practice for laboratory handling of potentially pyrophoric catalysts includes: storage in tightly closed containers; extreme care in transfer operations, with provision for immediate cleaning up of spills and copious water flushing; avoidance of air-drying during filtration, and storage of residues under water; use of water-flush in case of ignition [1]. The later reference details precautions to prevent fires in catalysts discharged from industrial reactors [2].

Some examples are:
Dodecacarbonyltetracobalt, 3420
Nickel, : Magnesium silicate, 4820
See COPPER CHROMITE CATALYST HYDROGENATION CATALYSTS

PYROPHORIC IRON–SULFUR COMPOUNDS

1. Schultze, R. *et al.*, *Arbeitsschutz*, 1964, 194–196
2. Dodonov, Ya. Ya. *et al.*, *Chem. Abs.*, 1964, **60**, 5058h –5059a
3. Anon., *Loss. Prev. Bull.*, 1977, (012), 1–6
4. Kletz, T. A., *Loss Prev. Bull.*, 1982, (048), 19–20
5. Bitay-Fulop, M. *et al.*, *Chem. Abs.*, 1979, **91**, 94069
6. Gendel, G. L. *et al.*, *Chem. Abs.*, 1982, **96**, 183813
7. Kyazimov, A. M. *et al.*, *Chem. Abs.*, 1982, **97**, 186029
8. Hempel, D. *et al.*, *Chem. Tech.* (Leipzig), 1983, **35**, 525–529
9. Walker, R. *et al.*, *Surf. Coating Technol.*, 1987, **31**, 163–197
10. Kostur, P. *et al.*, *Chem. Abs.*, 1988, **108** 97651

Iron(III) salts and thiols in alcoholic solution interact to produce highly pyrophoric mixtures containing iron alkylsulfides, iron oxide, hydrates, sulfides and sulfur. Effects of variation in reaction conditions and structure of thiols upon pyrophoricity were examined. Treatment of the pyrophoric mixtures with nitrogen oxide to form nitrosyl complexes effectively deactivates them [1]. Laboratory treatment of hydrated iron oxides with hydrogen sulfide simulated the production of pyrophoric iron sulfides which frequently cause fires in petroleum refining operations. Presence of gasoline during sulfide preparation gave pyrophoric materials which retained their activity longer than when gasoline was absent [2]. Several petroleum refinery fires and incidents are detailed [3]. In the investigation of a petroleum storage tank explosion in 1936, it was noticed that disturbing the sulfide scale in a tank gave several sparks, one of which, trapped in the scale caused incandescence of about 5 seconds duration. This type of occurrence may have been the original ignition source [4]. An apparatus and method for assessing the pyrophoric activity of these deposits is described [5], and their laboratory preparation in presence of amines or polyethylene glycols has been studied [6]. There have been studies of the possibility of suppression of spontaneous ignition of Fe–S deposits by corrosion inhibitors [7] or by other means [8]. The factors affecting the type of pyrophoric deposit produced from rust and petroleum-derived hydrogen sulfide are discussed [9]. Measures to inactivate such deposits call for their slow oxidation with steam–air, or dilute oxygen–inert gas mixtures [10].

DropBooks

Some examples are:
2-Hydroxyethylamine, : Carbon dioxide, etc., 0943
Iron disulfide, 4401
Iron(II) sulfide, 4400
Iron(III) sulfide, 4404
Phthalic anhydride, 2899

PYROPHORIC MATERIALS

1. Kayser, E. G. *et al., Spontaneously Combustible Solids*–Literature Survey, Rept. 75-159, US Naval Weapons Center, (USNTIS AD-A019919), 1975
2. Carson, P. A., Mumford, C. J., *Loss Prev. Bull.* 1993, (109), 11; *ibid.*, (110), 9

Existing information on solids spontaneously combustible in contact with air or water has been reviewed, with 145 references. Data relevant to the causes and prevention of spontaneous ignition are included, as well as the application of mathematical treatments to the problem, and available testing methods for assessing relevant factors in natural and manufactured products are discussed [1]. A two part review of pyrophoric materials and precautions in handling them is given [2].

Separate treatment is given for the relevant groups:

ALKYLALUMINIUM DERIVATIVES, ALKYLBORANES, ALKYLHALOBORANES ■
ALKYLHALOPHOSPHINES, ALKYLHALOSILANES, ALKYLMETALS
ALKYLNON-METAL HYDRIDES, ALKYLPHOSPHINES, ALKYLSILANES
ARYLMETALS, BORANES, CARBONYLMETALS, COMPLEX ACETYLIDES
COMPLEX HYDRIDES, HALOACETYLENE DERIVATIVES
HEXAMETHYLNITRATODIALUMINATE SALTS, METAL HYDRIDES
NON-METAL HYDRIDES, ORGANOMETALLICS, PYROPHORIC ALLOYS
PYROPHORIC CATALYSTS, PYROPHORIC IRON–SULFUR COMPOUNDS
PYROPHORIC METALS

Individually indexed compounds are:

Bis(acrylonitrile)nickel(0), 2312
∗ 1,2-Bis(dichlorophosphino)ethane, 0797
Bis(trimethylsilyl) phosphonite, 2611
Bromodimethylborane, 0887
Calcium silicide, 3943
Cerium trisulfide, 3967
Chromium(II) acetate, 1493
Chromium(II) oxide, 4241
Cobalt(III) nitride, 4214
Cobalt(II) sulfide, 4218
Dicobalt boride, 0128
Dimethyl ethanephosphonite, 1732
Europium(II) sulfide, 4293
2-Furaldehyde, 1836
Indium(II) oxide, 4641
Iron(II) chelate of bis-*N,N′*-(2-pentanon-4-ylidene)-1,3-diamino-2-hydroxypropane, 3616

Iron(II) hydroxide, 4392
Iron(II) maleate, 1393
Lead pentaphosphide, 4881
Lithium diethylamide, 1686
Lithium–tin alloys, 4682
Magnesium hydride, 4463
Manganese(II) *N,N*-diethyldithiocarbamate, 3358
Manganese(II) sulfide, 4706
5-Methyl-1(1-methylethyl)-1,2,3-azadiphosphole, 2455
Molybdenum(IV) oxide, 4716
Osmium(IV) oxide, 4833
† Phosphorus, 4874
Plutonium bismuthide, 0231
Poly(cyclopentadienyltitanium dichloride), 1843
∗ Poly(difluorosilylene), 4330
Potassium antimonide, 4673
Potassium *tert*-butoxide, 1650
Potassium cyclopentadienide, 1846
Potassium diethylamide, 1685
Potassium octacyanodicobaltate(8−), 2880
Potassium–sodium alloy, 4646
Silicon oxide, 4828
∗ Silver isophthalate, 2887
Sodium diethylamide, 1688
Sodium germanide, 4418
Thorium dihydride, 4489
∗ Thorium oxide sulfide, 4826
Titanium dibromide, 0284
Titanium dihydride, 4490
Titanium diiodide, 4630
Titanium trichloride, 4158
∗ Tricyclopentadienyluranium tetrahydroaluminate, 3688
Tris(2,2′-bipyridine)chromium(0), 3875
Uranium carbide, 0562
Uranium(III) nitride, 4732
Uranium(IV) oxide, 4843
Zinc, 4927
Zirconium dibromide, 0285
∗ Zirconium oxide sulfide, 4827

See also METAL DUSTS (reference 3), THORIUM FURNACE RESIDUES

DropBooks

PYROPHORIC METALS

1. Feitknecht, W., *Conf. on Finely Divided Solids*, Commis l'Eán. Atom., Saclay, 27–29 Sept., 1967
2. Peer, L. H. *et al.*, *Mill & Factory*, 1959, **65**(2), 79

3. Anon., *Chem. Eng. News*, 1952, **30**, 3210
4. Breidenfeld, J., *Metall.*, 1954, **8**, 94–97
5. Koelman, B. *et al., Metal Progress*, 1953, **63**(2), 77–79
6. Popov, E. L. *et al., Chem. Abs.*, 1975, **83**, 135768
7. Evans, J. D. *et al., Powder Metall.*, 1976, **19**, 17–21
8. Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 157–172
9. Nedin, V. V.; Kostina, E. S., *Chem. Abs.*, 1977, **86**, 157758, 157759
10. Klabunde, K. J. *et al., Inorg. Synth.*, 1979, **19**, 59–86

Finely divided metal powders develop pyrophoricity when a critical specific surface area is exceeded; this is ascribed to high heat of oxide formation on exposure to air. Safe handling is possible in relatively low concentrations of oxygen in an inert gas [1]. Safe handling, storage, disposal, and fire fighting techniques for hafnium, titanium, uranium and thorium, and hazards of machining the 2 latter metals are discussed [2]. Dry finely divided tantalum, thorium, titanium, zirconium metals, or titanium–nickel, zirconium–copper alloys are not normally shock-sensitive. However, if they are enclosed in glass bottles which break on impact, ignition will occur. Storage of these materials moist and in metal containers is recommended [3].

Heat of combustion, thermal conductivity, surface area and other factors influencing pyrophoricity of aluminium, cobalt, iron, magnesium and nickel powders are discussed [4]. The relationship between heat of formation of the metal oxide and particle size of metals in pyrophoric powders is discussed for several metals and alloys including copper [5]. Further work on the relationship of surface area and ignition temperature for copper, manganese and silicon [6], and for iron and titanium [7] was reported. The latter also includes a simple calorimetric test to determine ignition temperature.

In a literature review with 115 references, factors influencing the pyrophoricity of metals are identified as particle size, presence of moisture, nature of the surface of the particle, heat of formation of the oxide or nitride, mass, hydrogen content, stress, purity and presence of oxide, among others. Static charge hazards, fire and explosion incidents, handling procedures and transport considerations are also discussed. References are given to reviews of incidents involving barium, beryllium, magnesium, paper, plutonium, polypropylene, thorium, titanium, zinc-rich coatings and zirconium [8]. Equations to calculate the lower ignition limits for explosive suspensions in air of aluminium, iron, magnesium, manganese, tantalum, tin and titanium powders have been derived. Results for the latter agree well with experimental findings [9]. The reaction residues from various metal atom syntheses (involving vacuum evaporation of cobalt, copper, chromium, iron, magnesium, manganese, nickel, palladium, platinum, tungsten, vanadium or zinc, and co-deposition with a ligand) are often pyrophoric, and suitable precautions are detailed [10].

Individually indexed pyrophoric metals are:
Barium, 0200
Cadmium, 3949
Caesium, 4254

Calcium, 3922
Cerium, 3961
Chromium, 4222
Cobalt, 4199
Europium, 4292
Hafnium, 4599
Iridium, 4643
Iron, 4388
Lead, 4882
Manganese, 4700
Nickel, 4820
Palladium, 4885
Platinum, 4887
Plutonium, 4888
Rhodium, 4892
Rubidium, 4889
Strontium, 4913
Tantalum, 4914
Technetium, 4915
Thorium, 4917
Titanium, 4919
Tungsten, 4925
Uranium, 4923
Vanadium, 4924
Zinc, 4927
Zirconium, 4928
See Aluminium amalgam, Bismuth plutonide

DropBooks

PYROTECHNICS

1. Hardt, A. P., in Kirk-Othmer, 1982, Vol. 19, 484–499
2. Wharton, R. K., *Proc. Int. Pyrotech. Semin.*, 1991, **16**, 514
3. Ullmann, 1993, *A22*, 437
4. Kirk Othmer, 1996, Vol. 20, 680
5. Jennings-White, C. *et al.*, *J. Pyrotech.*, 1995, (2), 72
6. Hatanaka, S. *et al.*, *Kayaku Gakkaishi*, 1997, **57**(5), 213 & 220

With the possible exception of delay fuses, any pyrotechnic mixture represents a hazard worthy of report. Although the cause of frequent accidents reviewed in [2], compositions intended to explode or deflagrate are generally outside the field of this work and few are listed. Numerous reviews and specialist texts exist and hundreds of patents appear yearly. The account [1] of the theory and practice of pyrotechnics contains much useful information on the performance and potential hazards of a great variety of oxidant–fuel combinations which burn very rapidly or explosively. Safety measures are found in [2]. Other reviews written from a functional viewpoint are found in [3] and [4]. Some hazardously incompatible pyrotechnic mixes are reported [5]. Detonability of pyrotechnic compositions has

been studied. Whistles and chlorate or perchlorate & aluminium containing noise compositions often show detonability. Most others don't [6].

Water

Gu, W. *et al., Kayaku Gakkaishi*, 1996, **57**(5), 204

There is some risk of pyrotechnic mixtures containing powders of magnesium, aluminium, their alloy, or zinc, igniting from exothermic reactions of the metal in damp storage. Some study of inhibitors is undertaken. Titanium seems relatively inactive.

QUALITATIVE ANALYSIS

See Lead(II) picrate, *also* Nitric acid: Metal salicylates

QUATERNARY OXIDANTS (QUATERNARY PERMANGANATES)

1. Author's comments
2. Leddy, B. P. *et al., Tetrahedron Lett.*, 1980, **21**, 2261–2262
3. Karaman, H. *et al., J. Org. Chem.*, 1984, **49**, 4509–4516
4. Bretherick, L., *J. Chem. Educ.*, 1987, **64**(2), A42–A44

In an attempt to find new oxidants which will function homogeneously in organic substrate/solvent systems, many salts with quaternary organic cations and oxidising anions have been prepared during recent decades. There is however an intrinsic problem associated with this approach in that the compounds so prepared are effectively complete fuel–oxidant systems at the molecular level, with the oxidising anions juxtaposed in the crystal lattice with the organic cations. There have been a number of instances of unheralded and violent decomposition with this type of compound, which taken together suggest that considerable caution is necessary in preparing, storing and using these potentially hazardous salts [1].

Of a series of quaternary permanganate salts examined as organic oxidants, those of the 'unsaturated' cations benzyltrimethylammonium, benzyltriethylammonium, methyltriphenylphosphonium, ethylenebis(triphenylphosphonium) and hexadecylpyridinium all decomposed explosively at ~80–90°C, and of tetraphenylarsonium at 120–130°C. The permanganate salts of the 'saturated' cations tetramethylammonium, tetraethylammonium and hexadecyltrimethylammonium decomposed passively at 80–100°C, and were approximately as effective oxidants as their explosive counterparts. The latter could be considerably stabilised for use by adsorption on alumina [2]. General methods for the preparation and purification of a series of 16 quaternary ammonium permanganates and of 13 quaternary phosphonium permanganates have been developed, and the properties, decomposition temperatures and solubilities in 4 organic solvents and in water are tabulated. Examination of the thermal instability and mode of decomposition of several of the salts leads to the conclusion that thermal stability of these salts is a matter of concern, and that the salts should be held only in small quantity and in cold storage at all times, and that care should be exercised whenever they are handled and transferred from one container to another. Benzyltriethylammonium permanganate appears to be the best choice for long term storage stability,

with dichloromethane as an appropriate reaction solvent [3]. Possible structures for more stable quaternary oxidant salts are discussed [4].

Individually indexed compounds are:
Benzyltriethylammonium permanganate, 3617
Benzyltrimethylammonium permanganate, 3342
1,2-Bis(triphenylphosphonio)ethane permanganate, 3899
N-Hexadecylpyridinium permanganate, 3827
Methyltriphenylphosphonium permanganate, 3784
Tetrabutylammonium hydrogen monoperoxysulfate, 3732
Tetrabutylammonium permanganate, 3729
Tetraethylammonium perchlorate, 3088
Tetraethylammonium periodate, 3090
Tetramethylammonium ozonate, 1753
Tetramethylammonium pentaperoxodichromate, 3103
Tetramethylammonium superoxide, 1751
Tetraphenylarsonium permanganate, 3848
Tetramethylammonium periodate, 1749
See DICHROMATE SALTS OF NITROGENOUS BASES
See also PERCHLORATE SALTS OF NITROGENOUS BASES
See other OXOSALTS OF NITROGENOUS BASES

RADICAL INITIATORS

1. Whitmore, M. W. *et al., J. Loss Prev.*, 1993, **6**(2), 95
2. Bravo, S. *et al., Chem. Eng. Progress*, 1994, **90**(7), 62
3. Anon., personal communication, 1999

PropBooks

Apart from their ability to promote reactions beyond control, when used in excess, many polymerisation 'catalysts' of this class are dangerously unstable, to weakly explosive, in their own right. A table of accelerating reaction temperatures, determined by various methods, is given for many of these. The two main classes, azoorganics and peroxides, are likely to destabilise each other and should not be stored together in bulk [1]. A paper treats of safe handling of radical initiators and other polymerisation catalysts [2]. In the aftermath of an incident on a speciality polymer plant, where many different monomers and initiation systems were employed, it came to light that sparks were frequently observed when sweeping the floor. It was recommended that the floor be cleaned wet in future [3].
See Ammonium peroxodisulfate
See also ACCELERATING RATE CALORIMETRY, SELF-ACCELERATING DECOMPOSITION TEMPERATURE

RANEY ALLOYS

See Aluminium–cobalt alloy
Aluminium–nickel alloys, 0055
See also HYDROGENATION CATALYSTS

REACTION SAFETY CALORIMETRY

1. *Proc. Int. Symp. Prev. Risks Chem. Ind.*, Heidelberg, ISSA, 1976
2. Hub, L., *Proc. 6th Symp. Chem. Proc. Haz. Ref. Plant Des.*, 39–46, Rugby, IChE, 1977
3. *See entry* HEAT FLOW CALORIMETRY
4. Grob, B. *et al.*, *Thermochim. Acta*, 1987, **114**, 83–90
5. Singh, J., *Process Safety Progress*, 1997, **16**(1), 43.

One of the sessions of the Symposium was largely devoted to presentation and discussion on the use of various experimental calorimetric methods for use in assessing possible hazards in chemical processing operations. The methods described covered a wide range of sample sizes and degrees of complexity:

Grewer, T. Adiabatic small-scale reaction test in Dewar, simple to operate.

Janin, R. Measurements of heat release by DSC and of pressure development in sealed microcapsules.

Lemke, D. Heat accumulation tests of medium scale samples of thermally unstable technical materials in adiabatic storage.

Schleicher, K. Survey of general hazard testing methods.

Eigenmann, K. Use of micromethods in DTA, DSC.

Hub, L. Medium-small-scale safety calorimeter, usable under isothermal, quasi-isothermal or adiabatic conditions.

Regenass, W. Medium-scale heat flow calorimeter for measurement of heat release and cooling requirements under realistic reaction conditions.

Schofield, F. Use of a range of tests to determine detonation capability, localised thermal decomposition, thermal stability of reaction masses and effects of prolonged storage; translation of these results to industrial-scale processing operations.

Berthold, W. Use of adiabatic autoclave to simulate possibilty of thermal explosion in large containers of reactive materials [1].

Use of medium-scale heat flow calorimeter for separate measurement of reaction heat removed via reaction vessel walls and via reflux condenser system, under fully realistic processing conditions, with data processing of the results is reported [2]. More details are given elsewhere [3]. A new computer controlled reaction calorimeter is described which has been developed for the laboratory study of all process aspects on 0.5–2 l scale. It provides precise data on reaction kinetics, thermochemistry, and heat transfer. Its features are exemplified by a study of the (exothermic) nitration of benzaldehyde [4]. A more recent review of reaction safety calorimetry gives some comment on possibly deceptive results. [5].

See CHEMICAL STABILITY/REACTIVITY ASSESSMENT

See also ACCELERATING RATE CALORIMETRY, ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY, DIFFERENTIAL SCANNING CALORIMETRY

REACTION SIMULATION

Wright, A. *et al.*, *Chem. & Ind.*, 1988, 114–118

A reaction simulation program, REACTION, which will run on a personal computer, and which is specifically adapted for the non-steady states prevailing in batch reactions, is described and illustrated by a typical reaction model. Among

uses of the program for rapidly studying reaction engineering, process optimisation, control systems, scale-up and staff training requirements, are included thermal stability and process safety studies.

REACTIVE METALS

Stout, E. L., *Los Alamos Sci. Lab. Rept.*, Washington, USAEC, 1957; *Chem. Eng. News*, 1958, **36**(8), 64–65

Safety considerations in handling plutonium, uranium, thorium, alkali metals, titanium, magnesium, and calcium are discussed.

REDOX COMPOUNDS

Compounds which contain both oxidising and reducing functions in close proximity on a molecular basis tend towards explosive instability, and usually with low energy of activation. Relevant types are salts of reducing bases with oxidising acids, and metal oxosalts with coordinated nitrogenous reducants.

See AMMINEMETAL OXOSALTS, OXOSALTS OF NITROGENOUS BASES

See also CHLORITE SALTS, PERCHLORATE SALTS OF NITROGENOUS BASES

and the individually indexed compounds:

(Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2614
Bis(hydrazine)diperchloratochromium(III) perchlorate, 4128
∗ Borane–bis(2,2-dinitropropylhydrazine), 0137
Copper(I) perchlorate, 4058
Copper(II) phosphinate, 4272
Diamminenitratocobalt(II) nitrate, 4202
Hydrazinium chlorate, 4010
Hydrazinium chlorite, 4008
Hydrazinium nitrate, 4549
Hydrazinium perchlorate, 4011
Hydroxylaminium nitrate, 4524
Hydroxylaminium perchlorate, 4005
Indium(I) perchlorate, 4014
Iron(II) perchlorate, 4062
Iron(III) phosphinate, 4394
Lead(II) nitrate phosphinate, 4468
Manganese(II) chlorate, 4087
Manganese(II) perchlorate, 4088
Mercury(I) chlorite, 4080
Pentaamminephosphinatochromium(III) perchlorate, 4053
Pentaamminephosphinatocobalt(III) perchlorate, 4050
Pentaamminethiocyanatoruthenium(III) perchlorate, 0520
Peroxyformic acid, 0420
∗ Phosphonium perchlorate, 4006

DropBooks

Potassium cyanide−potassium nitrite, 0527
∗ Potassium pentacyanodiperoxochromate(5−), 1810
Potassium tricyanodiperoxochromate(3−), 1044
Tetrahydroxotritin(2+) nitrate, 4525
∗ Tetrakis(hydroxymethyl)phosphonium nitrate, 1754
Tin(II) nitrate, 4750
Tin(II) perchlorate, 4109
Trihydrazinealuminium perchlorate, 0064
Trimethylhydroxylammonium perchlorate, 1323
∗ Triphenylphosphine oxide hydrogen peroxidate, 3755
OXYGEN BALANCE
DRUMS

REDOX REACTIONS

Incidents involving interaction of active oxidants and reducing agents, either by design or accident, are usually extremely energetic, and examples of such redox reactions will be found under the entries:

∗ (Benzenesulfinato-*S*)pentaamminecobalt(III) trichloro(perchlorato)-stannate(II), 2614
∗ Calcium hypochlorite, : Acetic acid, Potassium cyanide, 3924
Cerium, : Water, 3961
Copper(II) nitrate, : Ammonium hexacyanoferrate(II), 4279
Dibenzoyl peroxide, : Lithium tetrahydroaluminate, 3639
N,N-Dimethyl-4-nitrosoaniline, : Acetic anhydride, Acetic acid, 2980
Dinitrogen oxide, 4744
Dinitrogen tetraoxide, : Formaldehyde, 4747
Ethyl hydroperoxide, : Hydriodic acid, 0925
Hydrogen peroxide, : Lithium tetrahydroaluminate, 4477
Hydroxylamine, 4498
Hydroxylamine, : Oxidants, 4498
Lead(IV) oxide, : Carbon black, Chlorinated paraffin, Manganese(IV) oxide, 4834
Magnesium nitrate, : Tin(II) fluoride, 4693
Manganese(IV) oxide, : Calcium hydride, 4705
Molybdenum(VI) oxide, : Graphite, 4717
Nitric acid, : Formaldehyde, 4436
Nitric acid, : Formic acid, 4436
Nitric acid, : Formic acid, Urea, 4436
Nitric acid, : Metal thiocyanate, 4436
Oxalic acid, : Urea, 0725
Ozone, : Acetylene, 4846
Perchloric acid, : Iron(II) sulfate
Perchloric acid, : Sodium phosphinate, 3998
Perchloric acid, : Zinc phosphide, 3998
α-Phenylazobenzyl hydroperoxide, : Phenylhydrazine, 3609

Phosphinic acid, : Mercury(II) oxide, 4503
Phosphonium iodide, : Oxidants, 4515
Potassium nitrate, : Reducants, 4650
Potassium phosphinate, : Air, or Nitric acid, 4459
Silver nitrate, : Magnesium, Water, 0022
Sodium chlorite, : Phosphorus, 4038
Sodium hypochlorite, : Formic acid, 4037
Sodium nitrate, : Arsenic trioxide, Iron(II) sulfate, 4721
Sodium nitrate, : Sodium phosphinate, 4721
Sodium nitrate, : Sodium thiosulfate, 4721
Sodium nitrate, : Tris(cyclopentadienyl)cerium, 4721
Sodium nitrite, : Potassium thiocyante, 4720
Sodium nitrite, : Sodium disulfite, 4720
Sodium nitrite, : Sodium thiocyanate, 4720
Sodium thiosulfate, : Sodium nitrite, 4804
1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide, : Lithium tetrahydroaluminate, 3312
Thallium(III) nitrate, 4762

See also METAL NITRATES: Esters, or Phosphorus, or Tin(II) chloride
METAL NITRATES: Metal phosphinates
METAL PERCHLORATES: Calcium hydride
PERCHLORATES: Reducants

See related UNIT PROCESS OR UNIT OPERATION INCIDENTS

REDUCANTS

DropBooks

Most of the compounds showing powerful reducing action have been listed separately under the group headings:

See also COMPLEX HYDRIDES, METAL ACETYLIDES, METAL HYDRIDES

The remaining individually indexed compounds are:

Aluminium, 0048
Ammonium phosphinate, 4554
Barium phosphinate, 0210
† Benzaldehyde, 2731
1,4-Benzenediol, 2333
∗ Bis(hydrazine)tin(II) chloride, 4070
Calcium acetylide, 0585
Calcium phosphinate, 3931
Chromium(II) chloride, 4052
Chromium(II) oxide, 4241
Chromium(II) sulfate, 4244
Copper(I) bromide, 0265
Diacetatotetraaquocobalt, 1780
Diisobutylaluminium hydride, 3082
† 1,2-Dimethylhydrazine, 0955

1,2-Diphenylhydrazine, 3517
Dipotassium phosphinate, 4431
† Ethanedial, 0723
† Formaldehyde, 0416
Formic acid, 0418
Gallium(I) oxide, 4411
Glucose, 2518
† Hydrazine, 4520
Hydroxylamine, 4498
Hydroxylaminium phosphinate, 4555
Hyponitrous acid, 4470
Iron(II) chloride, 4061
Iron(II) hydroxide, 4392
Iron(II) sulfate, 4399
Lead(II) phosphinate, 4531
Lead(II) phosphite, 4535
Lithium dithionite, 4687
Magnesium, 4690
Magnesium phosphinate, 4517
Manganese(II) phosphinate, 4519
† Methylhydrazine, 0503
Phenylhydrazine, 2373
Phosphinic acid, 4503
Phosphonic acid, 4504
Phosphonium iodide, 4515
Potassium, 4645
Potassium hypoborate, 0163
Potassium phosphinate, 4459
Sodium disulfite, 4808
Sodium dithionite, 4807
Sodium hydride, 4444
Sodium hypoborate, 0164
Sodium phosphinate, 4473
Sodium thiosulfate, 4804
Sulfur dioxide, 4837
Tetraphosphorus hexaoxide, 4867
Tin(II) chloride, 4116
Tin(II) fluoride, 4331
Titanium(II) chloride, 4117
Titanium trichloride, 4158
Tungsten dichloride, 4119
Vanadium dichloride, 4118
Vanadium trichloride, 4159
Zinc, 4927
Zirconium(II) chloride, 4121
Zirconium trichloride, 4160

REFRACTORY POWDERS

Krivtsov, V. A. *et al., Chem. Abs.*, 1979, **90**, 125991

Of a series of powdered refractory compounds examined, only lanthanum hexaboride, hafnium carbide, titanium carbide, zirconium carbide, magnesium nitride, zirconium nitride and tin(II) sulfide were dust explosion hazardous, the 2 latter being comparable with metal dusts. Individual entries are:

Hafnium carbide, 0521
Lanthanum hexaboride, 0193
Magnesium nitride, 4698
Tin(II) sulfide, 4900
Titanium carbide, 0561
Zirconium carbide, 0565
Zirconium nitride, 4733

REFRIGERATORS

Hasenpusch, W., *CLB Chem. Labor, Biotech.*, 1995, 46(5), 212, 214

Explosions in laboratory refrigerators are fairly common, often because volatile solvents such as ether are below their upper flammable limit in a refrigerator, but not in a solvent cabinet. The domestic refrigerators usually employed are far from flame-proofed. This review discusses causes and recommends precautions.

See also FLAMMABILITY, FLASH POINTS

REPAIR AND MAINTENANCE

DropBooks

1. Sanders, R. E., *Management of Change in Chemical Plants*, Oxford, Butterworth-Heinemann, 1993.
2. Anon., *Loss Prev. Bull.*, 1992, **107**, 17

These activities may introduce many hazards, such as contaminants, materials of repair corrodible, combustible or catalytic in the given environment, blocked vents, open valves etc. into the restarted plant, while shutdown and startup are, in any event, the most dangerous periods. Many examples of reactive hazards thus introduced are to be found in [1]. Mutatis mutandis, this is also true of the laboratory; this Handbook contains many incidents consequent upon stopping a reaction and/or its agitation to sample, change cooling bath, etc.

If the shutdown for repair is enforced by equipment failure, and thus abnormal, risks are greater; an explosion and fire resulted from failure of the airblower in an operating cracking catalyst regeneration unit, which was then steamed through, vented to the air and allowed to cool for two days prior to opening to replace the catalyst, whereupon the mishap occurred. Investigation suggested that the steam had formed water gas and light hydrocarbons by reaction with coke on the catalyst, and that these had not vented, nor had air penetrated enough to burn off combustibles from the probably still hot catalyst [2].

See CATALYTIC IMPURITY INCIDENTS

ROCKET PROPELLANTS

1. Kirk-Othmer, 1965, Vol. 8, 659
2. Urbanski, 1967, Vol. 3, 291
3. *ACS 88*, 1969

All of the theoretically possible high-energy (and potentially hazardous) oxidant–fuel systems have been considered for use, and many have been evaluated, in rocket propulsion systems (with apparently the sole exception of the most potent combination, liquid ozone–liquid acetylene). Some of the materials which have been examined are listed below, and it is apparent that any preparative reactions deliberately involving oxidant–fuel pairs must be conducted under controlled conditions with appropriate precautions to limit the rate of energy release.

Many of the possible combinations below are hypergolic (will ignite on contact) or can be made so with additives. A few single compounds have been examined as monopropellants (alkyl nitrates, ethylene oxide, hydrazine, hydrogen peroxide), the two latter being catalytically decomposed in this application. Solid propellant mixtures, which are of necessity long-term storage stable, often contain ammonium or hydrazinium perchlorates as oxidants. The hazardous aspects of rocket propellant technology have been surveyed [3].

OXIDANTS	FUELS
Chlorine trifluoride	Alcohols
Dinitrogen tetraoxide	Amines
Fluorine	Ammonia
Fluorine oxides	Beryllium alkyls
Halogen fluorides	Boranes
Methyl nitrate	Dicyanogen
Nitric acid	Hydrazines
Nitrogen trifluoride	Hydrocarbons
Oxygen	Hydrogen
Ozone	Metal hydrides
Perchloric acid	Nitroalkanes
Perchloryl fluoride	Powdered metals
Tetrafluorohydrazine	Silanes
Tetranitromethane	Thiols

See also PROPELLANTS

ROSIN (complex mixture, mainly resin acids)

Dry finely divided rosin is a significant dust explosion hazard.

See entry DUST EXPLOSION INCIDENTS (reference 22)

ROSINATED PIGMENTS

Twitchett, H. J., *Chem. Brit.*, 1977, **13**, 437

These products, usually calcium or barium 'lakes' of acid azo-dyes co-precipitated with the abietates ('rosinates'), are subject to spontaneous ignition, either in the freshly ground state, or as bulk material in drying ovens while a little moisture remains.

See METAL ABIETATES

ROTANES **$(C_7H_4)_n$**

de Meijere, A. *et al., Angewand. Chem. (Int.)*, 1995, **34**(7), 781; *Chem. Eur. J.* 1995, **1**(2), 124

The cyclic oligomers of 3-(1,2-Ethylidene)penta-1,4-diyne-1,5-diyl, (n = 5,6,7,8), obtained by oxidative coupling of 1,1-Diethynylcyclopropane, are called 'exploding rotanes'. They live up to the name, being sensitive to heat, friction or shock and having some 6 kJ/g available energy (TNT; 4.3 kJ/g). Higher homologues (n = 9,10,12) are probably no more stable, but are not yet reported as exploding; lower would be still less stable but are not known. The pentamer demolished a melting-point apparatus when a melting point was attempted. The permethylated rotanes do not explode similarly, although at most a third of the energy of the spiropropanes would be attributable to the cyclopropane ring. There is no reason to suppose that rotanes which are not polyacetylenic are unstable.

See other ALKYNES

RUBBER

Air, Cotton

Jones, S., *Res. Rept. 137*, Buxton, Safety in Mines Res. Est., 1956

If compressed air leaks from a rubberised cotton hose and causes squealing vibration to occur, enough heat may be generated to cause ignition. Fires have been started by squealing of poorly patched hoses, and ignition sources have been caused by use of rubberised cotton gaskets (cut from used conveyor belting, etc.) in plain flanged joints.

Sodium chlorate

See Sodium chlorate: Aluminium, Rubber

Metal azides

Tanaka, J. *et al.*, *Chem. Abs.*, 1952, **46**, 11743h

During the preparation of cellular rubber by thermal decomposition of calcium, strontium or barium azides, various additives were necessary to prevent explosive decomposition of the azide in the blended mixture.

RUNAWAY REACTIONS

1. *Runaway Reactions, Unstable Products and Combustible Powders*, Symp. Ser. No 68, Rugby, IChE, 1981
2. Various authors, *J. Loss Prev.*, 1993 **6**(2)

DropBooks

3. *Safety and Runaway Reactions*, Smeder, B & Mitchison, N. (Eds.), EUR 17723 EN, European Commission, 1997

The 22 papers of the symposium [1] were presented under the headings: Theory, Laboratory Studies, Calorimetry (2 sessions), Applications. Several papers are devoted to individual instrumental methods of measuring and assessing potential for exothermic runaway reactions to develop. An issue of the *Journal of Loss Prevention in the Process Industries* is devoted to a variety of, mostly calorimetric, studies of runaway reactions [2]. The proceedings of a European Union Seminar in 1994 appear as a book, including hard data as well as debate about such matters as operator training [3].

Examples of runaway reactions may be found in the entries:
Aluminium chloride, Alkenes, 0062
Butyrolactone, Butanol, 2,4-Dichlorophenol, Sodium hydroxide, 1527
Chlorine, 4047
Dichloronitrobenzene, Aniline, 2103
2,4,-Dichloronitrobenzene, Acetic acid, Potassium fluoride, Dimethylacetamide, 2104
† Ethylene oxide, Glycerol, 0829
† Ethylene oxide, Ammonia, 0829
† Formaldehyde, Phenol, 0416
Nitric acid, Formic acid, Urea, 4436
Nitric acid, Nitrobenzene, Sulfuric acid, 4436
Nitric acid, 1-Nitronaphthalene, Sulfuric acid, 4436
Sodium molybdate, 4713
1,2,4,5-Tetrachlorobenzene, Sodium hydroxide, Solvent, 2079
2,4,6-Trichloro-1,3,5-triazine, 1038

See also CALORIMETRY

RUST

Rust (a complex hydrated basic iron carbonate) is one of the most common contaminants in non-stainless steel plant, and has been involved, usually catalytically, in many different types of hazardous incident.

See FRICTIONAL IGNITION OF GASES AND VAPOURS

See also THERMITE REACTIONS

Carbon disulfide: Air, Rust
Hydrogen sulfide: Rust
Hydrazine: Rust
Magnesium: Metal oxides (reference 3)

SAFE STORAGE OF CHEMICALS

Pipitone, D., (Ed.), *Safe Storage of Laboratory Chemicals*, New York, Wiley, 1984

This book in 2 parts and 9 chapters with 6 appendices covers all aspects of the requirements for safe storage of chemicals for laboratories. The first part consists of 5 chapters:

Steere, N. V. Storage requirements for flammable and hazardous chemicals.

Bretherick, L. Incompatible chemicals in the storeroom: identification and segregation.

Nicholls, L. J. Labeling unstable chemicals.

Pipitone, D. A. Counteracting chemical spills in the storeroom.

Macenski, A. G. Use and selection of computers for chemical tracking systems.

The second part of the book contains 4 chapters on case histories and studies relating to chemical storage, and the appendices deal with specific aspects of labeling, purchasing chemicals, microcomputing, safety equipment, flash points of solvents and a safety checklist. A revised second edition is in press.

SAFETY LITERATURE

Many of the proliferating compendia of chemical safety information are composed in an unthinking, formulaic and plagiaristic manner, by persons or machines knowing no chemistry, giving rise to ramifying errors. These are usually on the side of safety (but not always so). An example in both the major multi-volume English language works was, until recently, the section: 'heating to decomposition'. Thus both reported sodium azide as giving nitrogen oxides, in which case car air-bags, which work by heating sodium azide to decomposition, must be extremely dangerous, both by virtue of the highly poisonous fumes discharged into the passenger compartment and by probable radiation from the nuclear transmutation evidently involved. There is a persistent inability to distinguish between pyrolysis and combustion combined with an automatic assumption that both give rise to the oxides of the elements present (except those of halogens) and to nothing else. Many nitrogenous compounds give much more hydrogen cyanide, even in circumstances of combustion, but this is rarely, if ever, mentioned (nor, apparently, are elemental halogens ever evolved when chlorine and bromine containing materials are burnt). Nitrogen oxides most commonly arise from heating empty air, and air is also omitted from consideration those entries which report common (combustible) solvents exploding on heating. Some of these errors have been copied into safety data sheets issued by supposedly authoritative chemical societies. Even as one source of error is moderated, another hastens to replace it.

This handbook, too, may contain errors while certainly holding reports, accident explanations and claims of hazard which the editor does not believe (usually indicated in phraseology or cross-reference). Nor is it automatically to be assumed that all listed and cross-indexed components of complex mixtures contributed to the accidents reported. Accept nothing uncritically!

DropBooks

SAMPLE DISSOLUTION

1. Bock, R., *Handbook of Decomposition Methods in Analytical Chemistry*, (Marr, L., translator and reviser), Glasgow, International Textbook Co., 1979
2. IUPAC Anal. Chem. Div., *Pure Appl. Chem.*, 1984, **56**, 479–489
3. Kingston, H. M. *et al., Anal. Chem.*, 1986, **58**, 2534–2541
4. Tattersall, P. J., *Lab. Practice*, 1986, **35**(10), 95

5. Bedson, A., *Chem. Brit.*, 1986, **22**, 894
6. Nakashima, S. *et al., Analyst* (London), 1988, **113**, 159–163
Of the 444 pages, 165 deal with oxidising procedures for analytical samples, and the hazards involved are detailed with suitable precautions [1]. The use of acid pressure decomposition methods in trace element analysis is reviewed (61 references). Vessels of high purity materials (PTFE, glassy carbon) within compact metal pressure casings are used. At 170°C, the temperature and considerable autogenous pressure enhance greatly the reaction capacity of acids and oxidising agents, permitting rapid dissolution of a wide range of samples. Critical aspects of vessel design and operational use are detailed [2]. The use of microwave heating to heat closed Teflon PFA vessels containg organic samples and various mineral acids has been investigated, with measurement of temperature profiles in the digestion vessels [3]. The technique has also been applied to other agricultural samples [4]. Use of microwave oven heating to accelerate sample dissolution has been reviewed [5]. Comparative tests on sealed and pressure-relieved digestion vessels with microwave heating have been reported, with nitric–perchloric acid mixtures to digest marine biological samples, and with hydrofluoric–nitric–perchloric acid mixtures to digest marine sediments [6].

Some examples of incidents are detailed under:
Hydrogen peroxide, : Organic materials, Sulfuric acid, 4477
Nitric acid, : Organic matter, Sulfuric acid, 4436
Perchloric acid, : Nitric acid, Organic materials, 3998
Potassium chlorate, : Nitric acid, Organic materials, 4017
See also MICROWAVE OVEN HEATING

SCALE OF WORK

1. Editor's comments
2. Gygax, R. W., *Chem. Eng. Progress*, 1990, (Feb.), 53
3. *Chemical Reaction Hazards*,, Barton, J. & Rogers, R., Rugby, IChE, 1993
4. Anon., *Loss Prev. Bull.*, 1992, (105) 15
5. *Org. Proc. Res. Dev*.
Nothing is so explosive that 1 mg is a significant danger. But with 1 tonne of sodium bicarbonate (baking soda), injudiciously mixed with weak acid (vinegar), it is quite possible to blow a reactor apart, with consequent fatalities. This consideration should be held in mind when using this text. Educators might also consider that, though they will have no accidents if they arrange practical work exclusively on the micro-scale, they will create very dangerous graduates who have no idea how to handle danger, nor even where it may lie, should they enter the world of real chemistry.

The problems of scale-up generally arise from the transfer of heat through the walls of a vessel, or the egress of gases and vapours through a hole in the wall. Rates of both of these, being surface phenomena, increase as the square of the linear dimensions of similar vessels. However, the contents, and associated potential energies, increase as the cube. It is also the case that the pressure a

vessel can contain decreases sharply with size if similar materials of construction are used [1].

For a study of methods of assessment of thermal runaway risk from laboratory to industrial scales [2]. A more detailed but eminently clear treatment of this and other needful safety considerations on scaling reactions up to production has since been published [3]. So slight a scale-up as replacing two charcoal filters by one bigger one may cause a fire because heat loss was reduced [4]. A journal largely devoted to scale-up of organic chemical processes has been launched [5].

Heat, and sometimes gas, transfer from the core of a bulk material, also influences auto-ignition and explosion. The concept of critical mass is not limited to nuclear explosives (though shape is also important). Some entries in this text, such as sodium chlorate, ammonium nitrate and ammonium perchlorate, have proved extremely destructive during industrial storage by the tens of tonnes, but are incapable of explosion at the ten gramme scale. Many other entries are for hazards significant only beyond laboratory scale [1].

See also ASSESSMENT OF REACTIVE CHEMICAL HAZARDS

SELF-ACCELERATING DECOMPOSITION TEMPERATURE (SADT)

Fisher, H. G. *et al., J. Loss Prev.*, 1993, **6**(3), 183

SADTs, a measure of safe storage and drying temperatures for industrial products, are determined by a variety of techniques, often large scale with up to 200 kg samples. Smaller scale calorimetric methods are discussed.

See also CALORIMETRY, SELF-HEATING AND IGNITION INCIDENTS

DropBooks

SELF-ACCELERATING REACTIONS

Brogli, F. *et al., Proc. 3rd Int. Symp. Loss Prev. Safety Prom. Proc. Ind.*, 665–683, Basle, SSCI, 1980

The general characteristics, contributory factors and potential hazards arising from self-accelerating (sometimes autocatalytic) reactions are discussed, together with the means to identify such reaction systems and appropriate practical precautions. Five product classes showing dangerous self-acceleration tendencies are aromatic nitro compounds, aliphatic *N*-nitroso compounds, thiophosphate esters, acrylates (and acrylonitrile and acrylamide), and sulfones or esters and chlorides of sulfonic acids. Four types of reaction similarly assessed are organic reactions with metals (Béchamp, Grignard), Bucherer amination, Friedel-Crafts with nitro compounds, and condensations with cyanuric chloride. 11 Examples of hazardous chemicals or reaction mixtures discussed in detail are the entries:

Aluminium chloride, : Nitrobenzene, 0062
Ammonium hydrogen sulfite, 4545
Benzyltriethylammonium permanganate, 3617
Bis(4-hydroxyphenyl) sulfone, 3497
2-Chloro-5-nitrobenzenesulfonic acid, 2144
1,3-Dichloro-5,5-dimethyl-2,4-imidazolidindione, 1865
† Dimethyl sulfoxide, 0921

† Methyl acrylate, 1531
N-Methyl-*N*-nitrosourea, 0875
Nitric acid, : 2-Aminothiazole, Sulfuric acid, 4436
3-Nitrobenzenesulfonic acid, 2268
Sodium hydride, : Dimethylformamide, 4444
Succinodinitrile, 1433
Sulfuric acid, : 4-Chloronitrobenzene, Sulfur trioxide, 4479
2,4,6-Trichloro-1,3,5-triazine, 1038
2,4,6-Trichloro-1,3,5-triazine, : Acetone, Water, 1038

SELF-HEATING AND IGNITION INCIDENTS

1. Virtala, V. *et al., Chem. Abs.*, 1952, **44**, 7770i −7771b
2. Napier, D. H. *et al., Runaway Reactions*, 1981, Paper 2/F, 1−15
3. Bishop, R. C., *Runaway Reactions*, 1981, Paper 2/H, 1−4
4. Duane, T. C. *et al., Runaway Reactions*, 1981, Paper 2/J, 1−8
5. Kotoyori, T. *et al., Thermochim. Acta*, 1983, **67**, 35−44
6. Bowes, P. C., *Self-Heating: Evaluation and Control*, London, HMSO, 1984

Methods for assessing the potential for oxidative self-heating and ignition of a range of 25 organic liquids and solids were described. Case histories are included for ignition of castor oil on peat, mineral oil on iron turnings, and wood shavings as lagging round steam pipes at 100°C, with 56 references [1]. Oxidative self-heating behaviour in mixtures of beech sawdust and raw linseed oil, in presence or absence of water (which accelerates heating) was studied to gain insight into the basic processes involved in ignition of such 2-phase systems [2]. Self-ignition phenomena in powdered grain products, corrugated fibreboards, iron powder, contaminated mineral lagging, and tobacco [3], and also spray drying of milk powder [4] were studied. A new adiabatic self-heating process recorder allows very strictly adiabatic self-heating tests to be carried out accurately and easily on small samples of a wide range of chemical materials [5]. A new book reviews the theoretical background and practical applications of methods of assessing the phenomena [6].

Some self-heating and ignition incidents will be found in the entries:
Adipic acid, 2441
1,4-Benzoquinone, 2214
† 1,3-Butadiene, 1480
Cinnamaldehyde, 3134
Copper iron(II) sulfide, 4269
Dibromomethylborane, 0426
† Di-*tert*-butyl peroxide, 3074
Dichlorine oxide, : Hydrocarbons, 4095
∗ Dimethyl terephthalate, 3292
† Hydrogen sulfide, : Soda-lime, 4483
Iron, : Air, Oil, 4388
Iron disulfide, 4401
∗ Methoxy-1,3,5,7-cyclooctatetraene, 3149

Nitric acid, : Ion exchange resins, 4436
1-Nitroso-2-naphthol, 3250
Sodium dichromate, : Sulfuric acid, Trinitrotoluene, 4250
Sodium nitrite, : Paper, Sulfur, 4720
ALDEHYDES
CELLULOSE NITRATE: Iron red, etc.
MILK POWDER
POLYPROPYLENE POWDER
SOAP POWDER
IGNITION SOURCES, INSULATION

SILANES **$H(SiH_2)_nH$, $RSiH_3$, etc.**

1. Stock, A. *et al., Ber.*, 1922, **55**, 3961
2. Kirk-Othmer, 1983, Vol. 20, 888
3. Ullmann, 1993, **A24**, 31 & 35

All the lower silanes are extremely sensitive to oxygen and ignite in air. The liberated hydrogen often ignites explosively [1]. Only under certain critical experimental conditions can they be mixed with oxygen without igniting [2]. Alkyloxysilanes can disproportionate to give silanes under base catalysis. Poly(alkyl)oxasilanes may depolymerise and disproportionate to give alkylsilanes and poly(alkyl)oxosiloxanes [3].
See Oxygen: Tetramethyldisiloxane

Chloroform, or Carbon tetrachloride, Oxygen
Stock, A. *et al., Ber.*, 1923, **56**, 1087
The chlorination of the lower silanes by halogenated solvents proceeds explosively in presence of oxygen, but catalytic presence of aluminium chloride controls the reaction.

DropBooks

Halogens
Stock, A. *et al., Ber.*, 1919, **52**, 695
Reaction of silanes with chlorine or bromine is violent.

Olefins, Platinum
Mathias, L. J. *et al., Chem. Abs.*, 1995, **124**, 286890v
Si−H bonds add across olefins over platinum catalysts. This reaction (hydrosilation) is used in silicone polymer manufacture, when the silane is a hydrogen bearing oligo(alkylsiloxane). With some types of olefin there have been reports of runaways to explosion because of unexpectedly fast reaction. Dangerous substrates recorded are 2-allylphenols and ethenylsiloxanes. Very low levels of catalyst (ppm) and good cooling are recommended.
See also VINYLSILOXANES

Individually indexed compounds are:
∗ Azidosilane, 4501
† Disilane, 4569

∗ Disilyl oxide, 4565
∗ Disilyl sulfide, 4568
∗ Oxodisilane, 4530
∗ Oxosilane, 4476
∗ Poly(silylene), 4487
† Silane, 4539
† Tetramethoxysilane, 1764
Tetrasilane, 4584
∗ Tetrasilylhydrazine, 4585
† Trisilane, 4579
∗ 2,4,6-Trisilatrioxane, 4566
∗ Trisilylamine, 4580
∗ Trisilylarsine, 0102
∗ Trisilylphosphine, 4583

See other NON-METAL HYDRIDES

SILICON COMPOUNDS

Groups or substances falling within this class are:

ALKYLHALOSILANES, ALKYLSILANES
HALOSILANES, ORGANOSILYL PERCHLORATES
SILANES, SILICONE GREASE, SILICONE LIQUID, SILICONE OIL
SILYLHYDRAZINES, TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES

SILICONE GREASE

Bromine trifluoride
See Bromine trifluoride: Silicone grease

SILICONE LIQUID **Poly(dimethylsiloxane)**

Silica powder, Unstated salt
Anon., *Loss Prev. Bull.*, 1987, (078), 9
A cosmetic preparation involved the vigorous dispersion of finely divided silica, and that of an ionically dissociable powder in a volatile silicone fluid. Small scale laboratory tests were uneventful, but in a preliminary 150 l manufacturing run, crackling noises were heard during the dispersion of silica powder, and on heating, the evolved vapour ignited. It was found that surface potentials of 35 kV could be measured 150 mm above the liquid. The static generation problem was completely eliminated by first dispersing the powdered salt component in the silicone liquid which effectively reduced the insulating properties of the silicone liquid.
See ELECTROSTATIC HAZARDS

SILICONE OIL

Yasufuku, S., *Chem. Abs.*, 1982, **96**, 220130

A major factor in ignition of dimethylsilicone oils after heating is the presence of a cyclic trimer. Flash point can be improved by addition of cerium acetylacetonate.

Contaminants

D'Onofrio, E. J., *Chem. Eng. News*, 1978, **56**(45), 51

Contamination of silicone oil baths with alkaline or acidic materials may lead to depolymerisation and a marked lowering of the flash point. This happened when the alkaline contents of a beaker heated in a silicone bath at 260°C frothed over into the oil, which itself then frothed and overflowed, exposing the electric immersion heater element which ignited the decomposition products.

Nitric acid

See Nitric acid: Silicone oil

SILVER COMPOUNDS

Many silver compounds are explosively unstable and/or powerful oxidants.

See METAL ACETYLIDES

Individually indexed compounds are:

Bis(2-aminoethyl)aminesilver nitrate, 1773
∗ Cyclopentadiene–silver perchlorate, 1859
Diamminesilver permanganate, 0018
Dihydrazinesilver nitrate, 0019
Dipyridinesilver(I) perchlorate, 3267
Disilver cyanamide, 0305
Disilver diazomethanide, 0306
Disilver ketenide, 0570
Disilver ketenide–silver nitrate, 0571
Disilver pentatin undecaoxide, 0036
∗ Heptasilver nitrate octaoxide, 0047
Nitrogen triiodide–silver amide, 4634
1,3-Pentadiyn-1-ylsilver, 1815
Pentasilver diamidophosphate, 0046
Pentasilver orthodiamidophosphate, 0044
Phenylsilver, 2217
Silver acetylide, 0568
∗ Silver acetylide–silver nitrate, 0569
Silver–aluminium alloy, 0002
Silver amide, 0015
Silver 5-aminotetrazolide, 0392
Silver azide, 0023
Silver azide chloride, 0009
Silver 2-azido-4,6-dinitrophenoxide, 2075
∗ Silver azidodithioformate, 0303
Silver 1-benzeneazothiocarbonyl-2-phenylhydrazide, 3605
Silver benzo-1,2,3-triazole-1-oxide, 2127

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Silver bromate, 0007
Silver buten-3-ynide, 1408
Silver chlorate, 0011
Silver chloride, 0008
Silver chlorite, 0010
∗ Silver chloroacetylide, 0566
∗ Silver cyanate, 0300
Silver cyanide, 0299
Silver cyanodinitromethanide, 0567
Silver 3-cyano-1-phenyltriazen-3-ide, 2670
Silver cyclopropylacetylide, 1838
Silver difluoride, 0014
Silver dinitroacetamide, 0689
Silver 3,5-dinitroanthranilate, 2642
Silver fluoride, 0013
Silver fulminate, 0301
Silver hexahydrohexaborate(2−), 0027
Silver hexanitrodiphenylamide, 3429
Silver 1,3,5-hexatrienide, 2052
Silver 3-hydroxypropynide, 1088
Silver hyponitrite, 0031
Silver imide, 0030
Silver iodate, 0020
∗ Silver isophthalate, 2887
Silver malonate, 1071
∗ Silver 3-methylisoxazolin-4,5-dione-4-oximate, 1409
Silver nitrate, 0022
Silver nitride, 0038
∗ Silver 4-nitrophenoxide, 2126
Silver *N*-nitrosulfuric diamidate, 0016
Silver osmate, 0034
Silver oxalate, 0572
Silver(I) oxide, 0032
Silver(II) oxide, 0025
Silver perchlorylamide, 0028
Silver *N*-perchlorylbenzylamide, 2734
Silver permanganate, 0021
Silver peroxochromate, 0037
Silver phenoxide, 2218
Silver phenylselenonate
Silver phosphinate, 0017
Silver sulfide, 0026
Silver tetrafluoroborate, 0005
Silver tetrafluorobromate, 0006
Silver tetrazolide, 0366
Silver trichloromethanephosphonate, 0304

Silver trifluoropropynide, 1030
Silver trinitromethanide, 0302
Silver 2,4,6-tris(dioxoselena)perhydrotriazine-1,3,5-triide, 0039
Silver trisulfurpentanitridate, 0024
Tetrasilver diimidodioxosulfate, 0043
Tetrasilver diimidotriphosphate, 0042
Tetrasilver orthodiamidophosphate, 0041
∗ Tetrasulfurtetraimide–silver perchlorate, 0029
1,2,4-Triazolo[4,3-*a*]pyridine–silver nitrate
Trisilver tetranitride, 0040

See other HEAVY METAL DERIVATIVES

SILVER-CONTAINING EXPLOSIVES

1. Luchs, J. A., *Photog. Sci. Eng.*, 1966, **10**, 334
2. MacWilliam, E. A. *et al., Photog. Sci. Eng.*, 1977, **21**, 221–224

Silver solutions used in photography can become explosive under a variety of conditions. Ammoniacal silver nitrate solutions, on storage, heating or evaporation eventually deposit silver nitride ('fulminating silver'). Silver nitrate and ethanol may give silver fulminate, and in contact with azides or hydrazine, silver azide. These are all dangerously sensitive explosives and detonators [1]. Addition of ammonia solution to silver containing solutions does not directly produce explosive precipitates, but these are formed at pH values above 12.9, produced by addition of alkali, or by dissolution of silver oxide in ammonia [2].

See Silver nitrate: Ammonia, etc.

See also FULMINATING METALS, SILVERING SOLUTIONS, TOLLENS' REAGENT

DropBooks

SILVER-CONTAINING RESIDUES

1. Wakeford, D. H., *School Sci. Rev.*, 1978, **59**(209), 665–666
2. Perman, C. A., *Talanta*, 1979, **26**(7), 603–604

A simple and economical method for recovering silver residues by dissolution in used photographic fixer (thiosulfate) solution, then precipitation by addition of zinc powder, is detailed [1]. After the acid digestion phase of silver recovery operations, addition of ammonia followed immediately by addition of ascorbic acid as reducant gives a near-quantitative recovery of silver metal, and avoids the possibility of formation of silver nitride [2].

SILVERING SOLUTIONS

1. Smith, I. C. P., *Chem. & Ind.*, 1965, 1070; *J. Brit. Soc. Glassblowers*, 1964, 45
2. Ermes, M., *Diamant*, 1929, **51**, 62, 587
3. Loman, E., and Mylius, W., *Diamant*, 1929, **51**, 526, 42
4. Sivertz, C. *et al.*, Ger. Pat. 2 162 263, 1972

Brashear's silvering solution (alkaline ammoniacal silver oxide containing glucose) or residues therefrom should not be kept for more than 2 hours after preparation, since an explosive precipitate forms on standing [1]. The danger of explosion may

be avoided by working with dilute silver solutions (0.35 M) in the Brashear process, when formation of $Ag(NH_3)_2OH$ (and explosive $AgNH_2$and Ag_3N therefrom) is minimised. The use of Rochelle salt, rather than caustic alkali, and shielding of solutions from direct sunlight, are also recommended safeguards [2,3]. Addition of sodium gluconate or tartrate to ammoniacal silver salt–base mixtures inhibits the formation of fulminating silver [4].

See FULMINATING METALS, TOLLENS' REAGENT

SILVER–NITROGEN COMPOUND HAZARDS

Anon, *CISHC Chem. Safety Summ.*, 1978, **49**, 29

A silver-containing solution was basified with sodium hydroxide, and after filtration, ammonia solution was used to wash residual silver from the filter. Hydrazine sulfate was then added to precipitate metallic silver and when the mixture was heated it exploded. This may have been caused by formation of silver nitride and/or hydrazine–silver complexes, both of which are explosively unstable.

See FULMINATING METALS, SILVER-CONTAINING EXPLOSIVES, TOLLENS' REAGENT

See also Silver chloride: Ammonia

See also Silver nitrate: Ammonia, Sodium hydroxide

SILYLHYDRAZINES $(R_3Si)_2NNHSiR_3$, etc.

Oxidants

1. Wannagat, U. *et al.*, *Z. Anorg. Chem.*, 1959, **299**, 341–349
2. Wannagat, U. *et al.*, *Monats.*, 1966, **97**, 1157–1162

During analysis of a series of tris(organosilyl)hydrazines, treatment with 1 : 1 mixtures of nitric and sulfuric acids had caused explosive reactions [1]. Subsequently the hypergolic behaviour of a range of 20 silylhydrazines and congeners in contact with fuming nitric acid was examined. All di- or tri-silyl derivatives showed ignition delays of 10 ms or less, several also exploding after ignition. All the derivatives ignited on dropping into gaseous fluorine, and into conc. liquid ozone–oxygen mixtures, most also exploding in the latter [2].

The most reactive compounds are:

1,2-Bis(triethylsilyl)hydrazine, 3583
1,2-Bis(triethylsilyl)trimethylsilylhydrazine, 3696
1,2-Bis(trimethylsilyl)hydrazine, 2616
1,2-Bis(tripropylsilyl)hydrazine, 3777
Dilithium 1,1-bis(trimethylsilyl)hydrazide, 2595
1,2-Dimethyl-2-trimethylsilylhydrazine, 2047
Lithium 2,2-dimethyltrimethylsilylhydrazide, 2041
3,3,6,6-Tetraphenylhexahydro-3,6-disilatetrazine, 3852
Triethylsilyl-1,2-bis(trimethylsilyl)hydrazine, 3586
Tris(trimethylsilyl)hydrazine, 3230

See other *N*-METAL DERIVATIVES

SINTERED GLASS

The recent replacement, in many laboratories, of filter papers and Buchner funnels by sintered, or fritted, glass filters when isolating solids has increased explosion hazards in two ways. Firstly, fritted glass is an excellent surface on which to induce detonation by scraping a solid. Secondly, the sinters rapidly clog and are valuable enough to encourage cleaning with powerful oxidant reagents rather than disposal, sometimes resulting in explosions from reaction with solvent or other materials impregnating the frit. The editor also finds it difficult to clean the porous support such that contamination of subsequently filtered solid is avoided and impossible to recover as much product as from a filter paper.

See Nitric acid: Glassware, Hydrogen peroxide, 5-Bromo-4-pyrimidinone

See also CLEANING BATHS FOR GLASSWARE, FRICTIONAL INITIATION INCIDENTS

SLAG WOOL

Potassium permanganate

See Potassium permanganate: Slag wool

SMELT

1. Nelson, W., *Chem. Abs.*, 1973, **78**, 126458
2. Morgan, H. W. *et al.*, *Chem. Abs.*, 1967, **66**, 56874t
3. Anon., *Chem. Abs.*, 1967, **66**, 56876v
4. Duda, Z., *Chem. Abs.*, 1976, **84**, 32851
5. Kashtanov, V. S., *Chem. Abs.*, 1979, **91**, 41112
6. Shivgulam, M. *et al.*, *Pulp Pap. Can.*, 1979, **80**(9), 89–92
7. Gardner, H. S., US Pat. 4 194 124, 1980
8. Kohl, A. L. *et al.*, *Tappi J.*, 1986, **63**(9), 82–85
9. Gairns, S. A. *et al.*, *Pulp Pap. Can.*, 1996, **97**(6), 46

'Smelt', the residue from 'burning' (high temperature combustive evaporation, sometimes with submerged burners) of spent sulfite liquor from wood-pulp treatment and consisting largely of sodium sulfide and sodium carbonate, explodes violently on contact with water while still hot. The mechanism is discussed [1], and operational procedures to avoid the possibility of explosions are recommended [2,3]. A further possible cause of explosions is the generation of hydrogen and/or hydrogen sulfide at the high temperatures involved [4]. Equipment used for processing kraft liquor is classified on the basis of explosion and fire hazards [5]. Addition of sodium or potassium chloride to smelt reduces the eutectic m.p. and the tendency to spout plugging and dissolving tank explosions, but increases the corrosion rate [6]. Smelt–water explosions are suppressed by the radiochemical nucleation of bubbles. No explosions occurred when cold water was dropped into molten sodium chloride at 1000°C under γ-irradiation at 4300 rad/min [7]. The probability and intensity of explosions in smelt–water systems is reduced by increase in pressure and temperature [8]. Experiment shows that pyrolysis of liquors at high temperatures in non-oxidising atmosphere can generate char

PrepBooks

particles containing substantial levels of metallic sodium, from reduction of sodium carbonate by carbon. This char may be pyrophoric and will certainly evolve hydrogen on contact with water; this is suggested as the principal cause of explosions [9].

See SUPERHEATED LIQUIDS

SOAP POWDER

Anon., *Chem. Abs.*, 1935, **29**, 6759.7

General factors affecting spontaneous ignition of soap powders were discussed.

SODA–LIME **$NaOH.Ca(OH)_2$**

Hydrogen sulfide

Bretherick, L., *Chem. & Ind.*, 1971, 1042

Soda–lime, after absorbing hydrogen sulfide, exhibits a considerable exotherm (100°C) when exposed simultaneously to moisture and air, particularly with carbon dioxide enrichment, and has caused fires in laboratory waste bins containing moist paper wipes. Saturation with water and separate disposal in sealed containers is recommended.

SODIUM CARBOXYMETHYLCELLULOSE

Hydrogen peroxide, Iron(II) sulfate, Nitric acid

See Hydrogen peroxide: Iron(II) sulfate, Nitric acid, etc.

'SODIUM PERCARBONATE' **Various structures, below**

Acetic anhydride

1. Anon., *Lab. Accid. in Higher Educ.*, item 20, HSE, Barking, 1987
2. Author's comment, 1989

Mixing 'sodium percarbonate' with acetic anhydride led to explosive shattering of the flask [1], undoubtedly caused by the formation of acetyl peroxide. The name 'sodium percarbonate' has been used indiscriminately to describe 3 different compounds, all of which would react with acetic anhydride to give extremely explosive acetyl peroxide [2]. These are sodium monoperoxycarbonate, NaOCO**.**OONa, [4452-58-8]; sodium peroxydicarbonate, NaOCO**.**OOCO**.**ONa, [3313-92-6]; and sodium carbonate sesqui hydrogen peroxidate, NaOCO**.**ONa**.**$1.5H_2O_2$, [15630-89-4].

See other PEROXOACID SALTS

SODIUM PRESS

Blau, K., private comm., 1965

The jet of a sodium press became blocked during use, and the ram was tightened to free it. It suddenly cleared and a piece of sodium wire was extruded, piercing a finger, which had to be amputated because of severe necrosis. Sodium in a blocked die should be dissolved out in a dry alcohol.

See Potassium: Alcohols

SOLVATED OXOSALT INCIDENTS

1. Bretherick, L., *Chem. Eng. News*, 1983, **61**(50), 2
2. Raymond, K. N., *Chem. Eng. News*, 1983, **61**(49), 4
3. Wolsey, W. C., *J. Chem. Educ.*, 1973, **50**(6), A335
4. Cotton, F. A. *et al.*, *J. Amer. Chem. Soc.*, 1960, **82**, 2986
5. Sandstrom, M. *et al.*, *Acta Chem. Scand.*, 1978, **A32**, 610
6. Cook, R. E. *et al.*, *J. Chem. Res.*, 1982, (S) 267, (M) 2772
7. Forsberg, J. H., *Chem. Eng. News*, 1984, **62**(6), 33
8. Bretherick, L., *Chem. Eng. News*, 1990, **68**(22), 4

Several instances of apparently stable solvated metal perchlorates being converted by partial desolvation into explosively unstable materials indicate that this may be a more common potential hazard than has been realised [1]. Neodymium perchlorate tetra-solvated with acetonitrile (obtained by vacuum evaporation of the solution at ambient temperature) had not been found to be thermally- or shock-sensitive, but when vacuum dried at 80°C to the di-solvate, it exploded violently on contact [2]. Erbium perchlorate tetrasolvated with acetonitrile had likewise appeared stable, but when vacuum dried at 150°C to a glassy solid which still contained some solvent, it too exploded when scraped with a spatula [3]. Mercury(II) perchlorate hexa-solvated with DMSO appears stable [4], but when dried to the tetrasolvate, it is impact- and friction-sensitive [5]. The fact that the solvating species may also be water suggests that this is not a direct effect of a perchlorate oxidising an organic solvent. Thus, cobalt(II) perchlorate hexahydrate is a common commercial (and stable) chemical, but when overheated during final drying which converted it to a trihydrate, the latter exploded under slight impact, and was later shown to be endothermic [6]. It is suggested that there is a need for closer control and documentation of drying procedures for solvated metal perchlorates [1]. An incident is reported where a solution of a lanthanide metal perchlorate in acetonitrile detonated during heating under reflux [7].

DropBooks

A possible explanation of the reduced stability of the lower organic solvates may be connected with the effect of reduced solvation upon the oxygen balance of the salts. Uncolvated metal perchlorates have an apparent balance of +700%, and solvation with 4 mols of acetonitrile reduces this to −46.3%, and with 4 or 6 mols of DMSO to −43% and −28.6% respectively. Desolvation to 2.18 mols of acetonitrile, or to 2.0 mols of DMSO, would give products of zero oxygen balance, with maximum energy release potential [8].

These and related incidents are detailed under:

† Acetonitrile, : Lanthanide perchlorate, 0758
Chromium(III) perchlorate . 6 dimethyl sulfoxide
Cobalt(II) perchlorate hydrates, 4051

Erbium perchlorate, 4132
∗ Gallium perchlorate, 4135
Iron(III) perchlorate, 4134
Mercury(II) perchlorate . 6 (or 4)dimethyl sulfoxide
Neodymium perchlorate . 2 acetonitrile, 4148
Silver perchlorate, 0012

SOLVENT CABINETS

1. Anon., *Sichere Chemiearbeit*, 1997, **49**, 3
2. Editor's Comments

After standing unopened for about a week, an unventilated solvent cabinet exploded violently, starting a fire which burnt out the laboratory. This was considered to have been a vapour/air explosion, not one caused by peroxide accumulation. The source of ignition was not clear, it might have been reactive drying agents. It is stated that the consequences would not have been as serious had the cabinet been ventilated [1]. To judge by the picture, the cabinet was of thin steel, offering negligible protection against heating by external fire. If it was like most of the solvent cabinets and bins known to the editor, the catch will probably also have been internal and made of sparking metal (although this explosion was not initiated by opening). A slight seepage of flammable solvent vapour seeping past a stopper in an open laboratory will be immediately dispersed by the ventilation. In the unventilated cabinets in which solvents have lately been kept, it is claimed as a safety measure, slight seepages of vapour will accumulate until they can form a substantial, enclosed, volume of explosive gases. A solvent cabinet designed for safety would be ventilated, thermally insulated, of non-sparking construction, and with blow-out panels. The majority of those the editor has met are none of these: they are potential explosive charges waiting to blow their door into the face of some unfortunate who sparks the explosion by turning the (sparking) catch [2].

SPILLAGES

1. *How to Deal with Spillages of Hazardous Chemicals*, Poole, BDH Chemicals Ltd., 5th edn, 1986
2. Melvold, R. W. *et al., J. Haz. Mat., 1988, 17, 329*–335

A revised wall chart, with standardised disposal procedures for 396 toxic and hazardous chemicals, which is useful in the storeroom as well as in the laboratory [1]. A guidance manual has been developed by EPA in the US to assist in the selection and use of sorbent materials to control industrial spillages of hazardous liquids [2].

STARCH

NFPA 61A, Quincy (Ma), National Fire Protection Association, 1989

The new US fire code covers precautions to prevent fires or dust explosions in handling dried starch.

Energy of exothermic decomposition in range 260–340°C was measured as 0.461 kJ/g.

Cornstarch dust may be a dust explosion hazard.

See entry THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION (reference 2)

See DUST EXPLOSION INCIDENTS (reference 33)

Calcium hypochlorite, Sodium hydrogensulfate

See Calcium hypochlorite: Sodium hydrogensulfate, etc.

Nickel nitrate

See METAL NITRATES: organic matter

STATIC INITIATION INCIDENTS

1. Krämer, H., *Chem. Ing. Tech.*, 1982, **55**, 419–428
2. Schaperklaus, H., Brit. Pat. 2004 476, 1979
3. Cartwright, P., *Chemtech*, 1991, **21**(11), 682
4. Britton, L. G., *Plant/Oper. Progr.*, 1992, **11**(2), 56

The current state of knowledge of charge generation in flowing or sprayed liquids was reviewed with 20 references, and criteria to allow assessment of ignition hazards were presented [1]. The risk of static sparks from thermoplastic bags or sacks was reduced by printing a grid of conductive ink on the surfaces [2]. A review of static electrical problems in the chemical industry, with further references, is found in [3]. Minimum Ignition Energies, with especial reference to electrostatic ignition, with tables of these and electrical properties of organic materials, are covered in [4].

DropBooks

Ignition by static features in the entries:

∗ Bis(2-azidobenzoyl) peroxide, 3628
∗ Calcium hypochlorite, 3924
Calcium polysulfide, 3942
Chlorine dioxide, 4042
Chlorine, : Hydrogen(?), Sulfuric acid, 4047
† Chloroethylene, 0730
Ethyl acetate, 1618
Iron, : Polystyrene, 4388
Lead(IV) oxide, : Metals, 4834
Methylmercury perchlorate, 0433
Oxygen (Gas), : Biological material, Ether, 4831
Potassium chlorate, : Metal phosphinates, 4017
Potassium perchlorate, 4018
Sodium chlorate, : Paper, Static electricity, 4039
† Trichlorosilane, 4136
Tris(2,2′-bipyridine)chromium(II) perchlorate, 3874

See also ADHESIVE LABELS, IGNITION SOURCES, MINIMUM IGNITION ENERGY

STEAM EXPLOSIONS

Drumheller, D. S., *TOM MIX: A Computer Code for Calculating Steam Explosion Phenomena*, Rept. SAND-81-2520, Richmond (Va), USNTIS, 1982

A mathematical model of the processes leading to steam explosions has been developed for the contact of hot liquids or molten solids dropping into water.

See MOLTEN METAL EXPLOSIONS, SMELT, SUPERHEATED LIQUIDS, VAPOUR EXPLOSIONS

STEEL

1. Anon., *Fire Prot. Assoc. J.*, 1953, **21**, 53
2. Karim, G. A. *et al., J. Fire Sci.*, 1987, **5**, 272–285

Ignition can occur if steel wool (or a scouring pad) short-circuits the contacts of even a small dry-cell torch battery [1]. The ignition and combustion characteristics of steel wool, loosely packed in wire crates has been investigated in a heated air stream of 4 m/s. Autoignition temperatures above 377°C were recorded [2]. As a structural material, wet steel vessels can deplete the air within of oxygen by rusting, or by autoxidation of ferrous sulfide formed by contact with sulfur-containing materials. This has caused a number of deaths from asphyxiation and the sulfide has ignited several fires. Hydrogen evolution is possible especially in contact with acids. Iron being a good catalyst for many reactions, trouble can also spring from this cause.

See Magnesium chloride: Air, etc., Sulfur dichloride: Iron

Apricots

Ontario Ministry of Labour, Internet information alert, 1997

A worker was killed while venting a bulging 45 gallon steel drum of apricot concentrate with a grinder. A grinder, the ultimate sparking tool, is not suitable for cutting into bulging food containers, which are more usually pressurised with hydrogen from interior corrosion than by the products of bacterial decay. However, bulging drums can kill without ignition.

See DRUMS

Silicon dioxide

See Silicon dioxide: Steel

See also RUST

See other IGNITION SOURCES

STORAGE OF CHEMICALS

1. *See entry* SAFE STORAGE OF CHEMICALS
2. Anon., *Loss Prev. Bull.*, 1988, (084), 19–22
3. Armstrong, B. S., *Loss Prev. Bull.*, 1988, (084), 23–31

The book is an amplified version of papers presented at the 1982 ACS CHAS Div. Symposium on safe storage of laboratory chemicals. Chap. 2 deals with the segregation of incompatible reactive chemicals on a logical basis [1]. Two accounts

of chemical warehouse fires emphasise the severe problems which arise from lack of proper segregation in storage of chemicals [2,3].

AMMONIUM PEROXODISULFATE: SODIUM SULFIDE
EARTHQUAKE, SOLVENT CABINETS

STRAINED-RING COMPOUNDS

Some molecules with small distorted rings (of high strain energy) are explosively unstable. Individually entries are:

∗ 2-Azatricyclo[2.2.1.$0^{2,6}$]hept-7-yl perchlorate, 2368
† Azetidine, 1255
Benzvalene, 2289
Bicyclo[2.1.0]pent-2-ene, 1856
2-*tert*-Butyl-3-phenyloxaziridine, 3406
3-Chloro-1,3-diphenylcyclopropene, 3679
1-Chloro-2,3-di(2-thienyl)cyclopropenium perchlorate, 3388
Cyanocyclopropane, 1463
† Cyclopropane, 1197
† Cyclopropyl methyl ether, 1608
2,3:5,6-Dibenzobicyclo[3.3.0]hexane, 3633
3,5-Dibromo-7-bromomethylene-7,7a-dihydro-1,1-dimethyl-1H-azirino[1,2-a]indole, 3474
2,2′-Di-*tert*-butyl-3,3′-bioxaziridine, 3359
Dicyclopropyldiazomethane, 2824
1,4-Dihydrodicyclopropa[*b*, *g*]naphthalene, 3452
N-Dimethylethyl-3,3-dinitroazetidine, 2848
Dinitrogen pentaoxide, : Strained ring heterocycles, 4748
† 1,2-Epoxybutane, 1609
† Ethyl cyclopropanecarboxylate, 2437
2,2′-(1,2-Ethylenebis)3-phenyloxaziridine, 3707
† Methylcyclopropane, 1581
† Methyl cyclopropanecarboxylate, 1917
† Oxetane, 1222
Pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane-1,2-dicarboxylic acid, 3261
1,2,3,-4,5, or -5,6-Pentafluorobicyclo[2.2.0]hexa-2,5-diene, 2070
Poly([7,8-bis(trifluoromethyl)tetracyclo [4.2.0.$0^{2,8}$.$0^{5,7}$]octane-3,4-diyl]-1,2-ethenediyl), 3463
Prismane, 2294
Spiro(homocubane-9,9′−diazirine), 3127
Tetracyclo[4.3.$0^{3,5}$.$0^{4,6}$]nona-1,7-diene, 3125
3,6,9-Triazatetracyclo[6.1.0.$0^{2,4}$.$0^{5,7}$]nonane, 2398

See also FURAZAN *N*-OXIDES

STYRENE–BUTADIENE RUBBER

Emmons, H. W., *J. Appl. Polym. Sci.*, 1981, **26**, 2447–2457

DropBooks

Plioflex rubber heated to above 300°C may ignite spontaneously. The mechanisms of the thermal reactions involved are discussed.
See also RUBBER

SUGARS

Air, Base

1. Young, J. A., *Chem. Health & Safety*, 1998, **5**(1), 4
2. Nicloux, M., *Bull. Soc. Chim. Biol.*, 1928, **10**, 1135
3. Young, J. A., private communication, 1979
4. Bretherick, L, *Chem. & Ind.*, 1980, 164; *Chem. Brit.*, 1980, **16**, 184

A fatality from carbon monoxide poisoning is reported while cleaning out a milk tank with an alkaline cleanser [1]. Apparently autoxidation of reducing sugars, including lactose, can produce up to 3,000 ppm of carbon monoxide under moderately alkaline conditions [2]. This is only likely to be hazardous in confined spaces. Warnings of the possibility of poisoning in such circumstances from this curious, long known but little remembered, reaction had been given earlier [3], [4]. Although alkalis are much used in the sugar industry, sucrose is not a reducing sugar.

Yeast

Dilute solutions of all sugars are subject to fermentation, either by yeast or by other micro-organism, or enzymes derived from these, producing gases which can pressurise and burst sealed containers. Some micro-organisms will produce hydrogen or methane, adding a fire and explosion hazard
See YEAST, CELLULOSE: Water

SULFINYL AZIDES $ArS(O)N_3$

Maricich, T. J. *et al., J. Amer. Chem. Soc.*, 1974, **96**, 7771, 7776

Benzene-, *p*-nitrobenzene-, and *p*-toluene-sulfinyl azides are thermally unstable, decomposing explosively when warmed alone or as conc. solutions. They may be prepared safely and handled as solutions at −20°C or below. The isolated solids may be stored at −80°C, but benzenesulfinyl azide explodes at 11°C, and *p*-toluenesulfinyl azide at 8°C. Individually indexed compounds are:
Benzenesulfinyl azide, 2273
4-Nitrobenzenesulfinyl azide, 2204
4-Toluenesulfinyl azide, 2780
See other ACYL AZIDES

SULFONATION INCIDENTS

1. Anon., *Loss Prev. Bull.*, 1979, (030), 159
2. Brogli, F. *et al., Runaway Reactions*, 1981, Paper 3/M, 4–5, 9
3. Quinn, M. E. *et al., Chem. Abs.*, 1985, **102**, 208618

An unspecified sulfonation mass was being held at 160°C for 24 h to distil out water. After 22 h an exothermic reaction set in, and sulfur dioxide and sulfur trioxide were evolved in quantity. It was later found that catalytic impurities had reduced the decomposition temperature considerably [1]. The use of a bench scale heat flow calorimeter to determine safe operating limits for effective sulfonation (reaction unspecified) is described [2]. During start-up of a reactor for continuous sulfonation of an aromatic compound under conditions close to the region of high decompositional activity, a thermal explosion occurred in a pump and recirculation line. After full thermal investigation of the various contributory factors, it was concluded that the decomposition was too violent for emergency venting procedures to be effective, and alternative quenching and/or dumping systems were proposed [3].

See other GAS EVOLUTION INCIDENTS

Other sulfonation incidents will be found in the entries:

Chlorosulfuric acid, : Hydrocarbons, 3997
∗ 4-Hydroxy-3-nitrobenzenesulfonyl chloride, 2146
2-Methoxyanilinium nitrate, 2829
3-Nitrobenzenesulfonic acid, 2268
4-Nitrotoluene, 2764
Sulfuric acid, : Tetramethylbenzenes, 4479

See other UNIT PROCESS OR UNIT OPERATION INCIDENTS

SULFONIC ACID ESTERS RSO_2OR'

1. Collin, D. T. *et al., Chem. & Ind.*, 1987, 60
2. James, D. M., *Comprehensive Organic Chemistry*, Vol. 3, 342, Oxford, Pergamon, 1979
3. Dauben, W. G. *et al., J. Amer. Chem. Soc.*, 1968, **90**, 3835
4. Anon., private comm., 1989

DropBooks

During the distillation at 81–89°C/0.8 mbar of cyclobutylmethyl methanesulfonate from a bath at 120°C, there was a sudden and violent explosion. Thermal instability of the ester was confirmed by heating a small sample at 0.5°C/min, when rapid autocatalytic and exothermic decomposition occurred at 110°C. In an isothermal test at 65°C a sample decomposed vigorously after 48 h. The decomposition involves rapid elimination of cyclopentene, the residue being methanesulfonic acid and polymer. Promotion of the decomposition by presence of added traces of methanesulfonic acid, and inhibition by the presence of sodium hydrogen carbonate confirms a mechanism involving acid catalysis. The ester is also unstable in toluene at 110°C, and in *N,N*-dimethylacetamide or sulfolane at 120°C. If the ester must be stored, this should be done as a 20 wt% solution in *tert*-butyl methyl ether at 0°C in presence of 5 mol% of sodium hydrogen carbonate. Cyclobutyl 4-toluenesulfonate, cyclopentylmethyl methanesulfonate and 1-pentyl methanesulfonate when heated at 0.5°C/min showed similar but slightly less energetic decomposition at 118, 128, and 185°C, respectively [1]. Instability of sulfonates of secondary alcohols is well documented [2]. A sample (25 g) of cyclobutylmethyl 4-toluenesulfonate was prepared by a literature method [3]. Upon attempted vacuum distillation at

0.27 mbar from a 50 ml flask in an oil bath at ca. 150°C, a violent explosion occurred. A sample from a repeat preparation was examined by DSC and at 2°C/min vigorous exothermic decomposition occurred at 140°C [4]. It is calculated that some 3.9 l of cyclopentene vapour at 140°C would cause a pressure surge to 80 bar in a 50 ml closed vessel.

Individually indexed compounds are:
Cyclobutyl 4-methylbenzenesulfonate, 3404
Cyclobutylmethyl methanesulfonate, 2510
Cyclopentylmethyl methanesulfonate, 2867
1-Pentyl methanesulfonate, 2550
See also SULFUR ESTERS

SULFONYL AZIDES **RSO_2N_3**

See ACYL AZIDES

SULFUR BLACK

Anon., *Ind. Eng. Chem.*, 1919, **11**, 892
Twenty-four hours after several barrels of the dyestuff were bulked, blended and repacked, spontaneous heating occurred. This was attributed to aerobic oxidation of excess sodium polysulfide used during manufacture.
See Sodium sulfide *See other* SELF-HEATING AND IGNITION INCIDENTS

SULFUR COMPOUNDS

Groups and substances falling within this class are:
See also ALKANETHIOLS, ALKENEBIS(SULFONIUM PERCHLORATES) ALLYL TRIFLUOROMETHANESULFONATES, ARENEDIAZO ARYL SULFIDES BIS(ARENEDIAZO) SULFIDES, BIS(SULFURDIIMIDES DIAZONIUM SULFATES, DIAZONIUM SULFIDES AND DERIVATIVES METAL AMIDOSULFATES, METAL PHOSPHORUS TRISULFIDES METAL SULFATES, METAL SULFIDES, NON-METAL SULFIDES SULFONIC ACID ESTERS, SULFUR BLACK, SULFUR ESTERS THIOPHENOXIDES, 'XANTHATES'

SULFUR ESTERS **$RSOR'$, $RSO.OR'$, RSO_2OR'**

The group name is intended to cover esters derived from sulfenic, sulfinic and sulfonic acids, some of which are thermally unstable. This is especially so for esters of unsaturated alcohols, which are also liable to polymerise, catalysed by the liberated acids. Individually indexed compounds are:
Allyl benzenesulfonate, 3155
Allyl 4-toluenesulfonate, 3315
Bis(trimethylsilyl) peroxomonosulfate, 2602
2-Buten-1-yl benzenesulfonate, 3316

3-Butyn-1-yl 4-toluenesulfonate, 3399
2-Chloro-2-propenyl trifluoromethanesulfonate, 1426
Cyclobutyl 4-methylbenzenesulfonate, 3404
Cyclobutylmethyl methanesulfonate, 2510
Cyclopentylmethyl methanesulfonate, 2867
Diallyl sulfate, 2443
Diethyl sulfate, 1710
Diethyl sulfite, 1709
1,10-Di(methanesulfonyloxy)deca-4,6-diyne, 3543
∗ Dimethyl selenate, 0930
† Dimethyl sulfate, 0929
Dimethyl sulfite, 0927
Ethyl 3,4-dihydroxybenzenesulfonate, 2988
Ethyl fluorosulfate, 0856
∗ 2-Isocyanoethyl benzenesulfonate, 3143
∗ *N*-Methyl-*p*-nitroanilinium 2(*N*-methyl-*N*-*p*-nitrophenylaminosulfonyl) ethylsulfate, 3713
1-Pentyl methanesulfonate, 2550
Prop-2-enyl trifluoromethanesulfonate, 1461
∗ Silyl trifluoromethanesulfonate, 0444
Trifluoroacetyl trifluoromethanesulfonate, 1057
3-Trimethylsilylprop-2-enyl trifluoromethanesulfonate, 2847
∗ Zinc ethylsulfinate, 1711
See ALLYL TRIFLUOROMETHANESULFONATES

DropBooks

SUNSPOTS

Ye, Y. *et al., Proc. 18th Int. Pyrotech. Semin.*, 1992, 1019
It is claimed that accidents in the Chinese pyrotechnic industry peak with the sunspot cycle

SUPERHEATED LIQUIDS

1. Reid, R. C., *Superheated Liquids, A Laboratory Curiosity and, Possibly, an Industrial Curse, Chem. Eng. Educ.*, 1978, 60–63, 83–87; 108–111, 127–129; 194–196, 203–206
2. Reid, R. C., *Science*, 1979, **203**(4386), 1263–1365

This comprehensive survey of the title topic is in three parts, the first dealing with the theoretical background and laboratory studies, with 29 references. The second part, with 21 references deals with case histories and experimental studies of industrial vapour explosions. These involved the systems molten titanium–water, molten copper–water, molten aluminium–water, smelt–water, water–various cryogenic liquids, molten salt–water and molten uranium dioxide–liquid sodium. In the third part (with a further 26 references) is discussion of the various theories which abound, and the general conclusion that superheated liquids most likely play a major role in all these phenomena [1]. A further related publication covers BLEVEs and pressure let-down explosions [2].

See LIQUEFIED GASES, LIQUEFIED NATURAL GAS, MOLTEN METAL EXPLOSIONS, SMELT, VAPOUR EXPLOSIONS

SUPERIORS/SUPERVISORS

Can be a source of hazard. Some may react violently to suggestions that they are not omniscient. Suggested reactions should never be undertaken without investigating safety factors, not even if the editor is the superior in question.

TETRAAZAMACROCYCLANEMETAL PERCHLORATES

Hung, Y., *Inorg. Synth.*, 1980, **20**, 112–113

The dichlorocobalt(IV) perchlorate salts complexed with [15] ane-N_4 and [16] ane-N_4 are described as potentially explosive.

See also POLYAZACAGED METAL PERCHLORATES, AMMINEMETAL OXOSALTS

TETRAHYDROPYRANYL ETHER DERIVATIVES

Meyers, A. I. *et al.*, *Tetrahedron Lett.*, 1976, 2417–2418

The tetrahydropyranyl group, commonly used in synthetic procedures to protect hydroxyl groups, appears not to be safe when peroxidising reagents are used with tetrahydropyranyl ether derivatives, because explosive peroxides, not destroyed by the usual reagents, are produced.

The hydroboration product of 2-methyl-2-propenyl tetrahydropyranyl ether was routinely oxidised with alkaline hydrogen peroxide, then treated with sodium sulfite solution during work-up. The product gave a negative test for peroxides but exploded violently during attempted distillation at 0.06 mbar from a vessel at 120°C. Epoxidation of 3-methyl-3-butenyl tetrahydropyranyl ether with peroxyacetic acid gave, after sulfite treatment, an apparently peroxide-free product. However, after distillation at 1 mbar, the fore-run (b.p. 40–70°C) exploded violently when the flask was disturbed. The main fractions were found subsequently to give strong positive indications for the presence of peroxides which were only removed after prolonged treatment with sodium thiosulfate. (There is some evidence to suggest that sodium sulfite may under certain circumstances actually promote peroxide formation.)

Other acetal-type protecting groups (tetrahydrofurfuryl ethers, methoxymethyl ethers, 1,3-dioxolanes) are also considered to be incompatible with oxidising agents.

See other PEROXIDISABLE COMPOUNDS

TETRA(*N*-METHYLPYRIDYL)PORPHINE PERCHLORATES

Reid, J. B. *et al.*, *Inorg. Chem.*, 1977, **16**, 968

Variously metallated derivatives of the porphine nitrate were converted to the perchlorate salts, but several exploded during drying. The need for great caution in attempting to prepare the anhydrous perchlorates is stressed.

See Tetrakis(4-*N*-methylpyridinio)porphinecobalt(III)(5+) perchlorate

See other AMMINEMETAL OXOSALTS

TETRAMETHYL [14] TETRAENE-N_8 METAL PERCHLORATES

Peng, S.-M. *et al.*, *Inorg. Chem.*, 1978, **17**, 120

The perchlorate salts of the complexes with divalent cobalt, nickel, and particularly iron (analogous to IV, p. S-15) are potentially explosive, and storage for more than 4 weeks is not advised.

See [14] DIENE-N_4 COMPLEXES, AMMINEMETAL OXOSALTS

TETRAZENES $R_2NN{=}NNR_2$

Houben Weyl, 1967, 10/2, 828

Several compounds of this class explode forcefully on heating, the tetramethyl and tetraallyl derivatives are specifically mentioned.

Individual compounds are:
1-Acetyl-4-(4′-sulfophenyl-3-tetrazene, 2982
1-Ethyl-1,1,3,3-tetramethyltetrazenium tetrafluoroborate, 2586
3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2804
Potassium 3,5-dinitro-2(1-tetrazenyl)phenoxide, 2256
Tetraallyl-2-tetrazene, 3545
Tetramethyl-2-tetrazene, 1759

See HIGH NITROGEN COMPOUNDS

TETRAZOLES HNN=NN=CH

PrOpBooks

1. Benson, F. R., *Chem. Rev.*, 1947, **41**, 4–5
2. Morisson, H., *Util. Elem. Pyrotech. Explos. Syst. Spatiaux, Colloq. Int. 1968* (publ. 1969), 111–120
3. Schroeder, M. A., *Rept. AD-A018652*, Richmond (Va.), USNTIS, 1975
4. Grimmett, M. R.; *Barton & Ollis*, 1979, Vol. 4, 364
5. Matsuzawa, T. *et al.*, *Loss Prevention and Safety Promotion in the Process Industries*, (Mewis, Pasman and De Rademaker: Eds), Vol II, 315, Amsterdam, Elsevier, 1995

There is a wide variation in thermal stability in derivatives of this high-nitrogen nucleus, and several show explosive properties [1]. The characteristics of explosive tetrazole salts have been summarised [2], and the relationship between structure and reactivity of isomeric 1- and 2-tetrazole derivatives has been reviewd in a ballistics context [3]. It is claimed that tetrazole diazonium salts detonate, in water, at concentrations little above 2%, at 0°C [4]. A sensitivity study has been made of numerous tetrazoles, their salts, and compositions thereof with oxidants, as gas generators for airbags. Salts are less sensitive than the parent tetrazoles. Mixtures with potassium perchlorate are both more energetic and more sensitive, those with potassium nitrate are usually similar, though some are less sensitive to electric discharge. In the absence of oxidants, hydrogen cyanide is a frequent decomposition product [5]. Individually indexed compounds are:

5-Amino-2-ethyl-2*H*-tetrazole, 1268
5-Aminotetrazole, 0461

5-Azidotetrazole, 0388
Barium 5,5′-azotetrazolide, 0577
1,6-Bis(5-tetrazolyl)hexaaza-1,5-diene, 0827
N-Chloro-5-phenyltetrazole, 2674
Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1429
5-Cyano-2-methyltetrazole, 1120
2(5-Cyanotetrazole)pentaamminecobalt(III) perchlorate, 0974
5-(Diazomethylazo)tetrazole, 0719
5-Diazoniotetrazolide, 0548
1-Dichloroaminotetrazole, 0371
1,2-Dihydropyrido[2,1-*e*]tetrazole, 1834
5-(4-Dimethylaminobenzeneazo)tetrazole, 3161
Disodium 5,5′-azotetrazolide, 1018
∗ Disodium 5,5′-azoxytetrazolide, 1019
Disodium 5-tetrazolazocarboxylate, 1012
Disodium tetrazole-5-diazoate, 0549
1,3-Di(5-tetrazolyl)triazene, 0778
Ethyl 2-cyano-2-(1-*H*-tetrazol-5-ylhydrazono)acetate, 2359
2-Ethyltetrazole, 1213
5-Ethyltetrazole, 1214
5,5′-Hydrazotetrazole, 0826
Lead 5,5′-azotetrazolide, 1020
Mercury 5,5′-azotetrazolide, 0980
Mercury(II) 5-nitrotetrazolide, 0981
2-Methyltetrazole, 0814
2-Methyl-5-vinyltetrazole, 1511
1-(2-Naphthyl)-3-(5-tetrazolyl)triazene, 3394
5-*N*-Nitroaminotetrazole, 0415
1-(2-Nitrophenyl)-5-phenyltetrazole, 3602
5-Nitro-2-picryltetrazole, 2638
5-Nitrotetrazole, 0387
∗ Pentazole, 4443
5-Phenyltetrazole, 2727
3-Phenyl-1-(5-tetrazolyl)-1-tetrazene, 2804
Potassium 1-tetrazolacetate, 1106
Silver 5-aminotetrazolide, 0392
Silver 1,3-di(5-tetrazolyl)triazenide, 0690
Silver tetrazolide, 0366
Sodium 5-azidotetrazolide, 0551
Sodium 5-(dinitromethyl)tetrazolide, 0681
Sodium 5(5′-hydroxytetrazol-3′-ylazo)tetrazolide, 0682
Sodium 5-nitrotetrazolide, 0547
Sodium 1-tetrazolacetate, 1119
1,3,4,6-Tetrakis(2-methyltetrazol-5-yl)-hexaaza-1,5-diene, 3013
Tetrazole, 0411
Tetrazole-5-diazonium chloride, 0370

5-Trichloromethyltetrazole, 0657
5-Trichloromethyl-1-trimethylsilyltetrazole, 1927
See other HIGH-NITROGEN COMPOUNDS

TEXTILE CLOTHING STATIC CHARGES

Wilson, N., *J. Electrost.*, 1977, **4**, 67–84
The clothing worn by a process operator insulated from earth may develop static charges far higher (up to 100-fold) than the minimum ignition energies for various flammable gas–air mixtures. This is true for a wide range of clothing materials including cotton. Dangerous levels of charge may be avoided by ensuring a low resistivity of the surface material worn outermost.
See other IGNITION SOURCES

THERMAL EXPLOSIONS

Verhoeff, J., *Experimental Study of the Thermal Explosion of Liquids*, Doctoral Thesis, University of Delft, 1983
In a study of the course of thermal explosions in low, high and constant pressure autoclave experiments, 3 stages of thermal runaway, initiation and explosion were identified and studied in detail. Most of the work was done with *tert*-butyl peroxybenzoate, but limited comparative examinations were carried out on 8 other energetic substances.

DropBooks

THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

1. Grewer, T., *Chem. Ing. Tech.*, 1975, **47**, 230–235
2. Hartgerink, J. W., *Proc. 3rd Symp. Chem. Probl. Connected Stab. Explos.* 1973, (publ. 1974), 220–230
3. Grewer, T., *Chem. Abs.*, 1980, **93**, 210923
4. Tyler, B. J., *Chem. Brit.*, 1981, **17**, 274, 276
5. O'Brien, G. J., *Chem. Eng. Progr.*, 1982, 78(1), 46–49
6. Fierz, H. *et al.*, *Chem. Engr.*, 1984, **400**, 9–10
7. Gibson, N., *Chem. & Ind.*, 1984, 209–211
8. Smith, C. D., *Chem. Eng. Progress*, 1994, **90**(9), 67

The importance of gaining knowledge on the reaction parameters of exothermic reaction systems to assess potential processing hazards is discussed in detail. The roles of DTA, adiabatic storage tests and adiabatic reaction tests were discussed, and suitable techniques described with reference to practical examples of thermally unstable systems [1]. Two storage tests (adiabatic storage and isothermal heat generation) were described which give information on the induction period of instability. An exothermal decomposition meter, with 100-fold higher sensitivity than DTA is described [2]. The importance of the relationship between reaction energy and reaction rate for batch reactions, and of the factors which may lead to reaction delays and instability, and of secondary reactions, are discussed and exemplified [3].

The safety margin between reaction stability and runaway may be as little as 10−20°C, and this may be diminished or eliminated by apparently minor changes (higher initial temperature or concentration, better catalysts, less stirring or cooling capacity) in processing conditions [4]. A standardised review procedure to identify and eliminate factors likely to lead to reaction instability is described [5]. Application of the bench scale heat flow calorimeter to the overall problems of ensuring stability in chemical processing operations is discussed with examples [6]. The advantages to be gained by using a range of tests to identify potential processing hazards are outlined [7]. Considerations of explosion and detonation are expounded. A quick simple scanning procedure for detecting self-heating to explosion is detailed, much cheaper than Accelerating Rate Calorimetry. There is also a test for transition from deflagration to detonation (though this will only detect materials of greater detonability than most explosives) [8].

See ASSESSMENT OF REACTIVE CHEMICAL HAZARDS, CALORIMETRY

THERMITE REACTIONS

1. Bond, 1991, 63
2. Gibson, N. *et al., Proc. 3rd Symp. Chem. Proc. Haz. Ref. Plant Des.*, 26−35, London, IChE, 1968
3. Britten, G. C., *School Sci. Rev.*, 1976, **57**(201), 732
4. Hadfield, J. M., *School Sci. Rev.*, 1980, **62**(219), 394
5. Bozzelli, J. W. *et al., J. Chem. Educ.*, 1979, **54**, 675−676
6. Roebuck, P. J., *Educ. Chem.*, 1979, **16**, 178−179
7. Ivanov, G. V. *et al., Chem. Abs.*, 1979, **91**, 76323
8. Billinge, K., *Fire Prev. Sci. Technol.*, 1981, (24), 13−19
9. Shidlovskii, A. A. *et al., Chem. Abs.*, 1983, **98**, 18942
10. Eastland, G. W., *J. Chem. Educ.*, 1984, **61**, 723
11. Zumdahl, S. S., *Chem. Eng. News*, 1990, **68**(20), 2
    Fawcett, H. *et al., CHAS Notes*, 1990, **VIII**(3), 2
12. Ismailov, M. B., *et al., Fizika Goreniya i Vzryva*, 1992, **28**(1), 46
    Filatov, B. M., *et al., ibid.* 53
13. Wright, S. W., *J. Chem. Educ.*, 1994, **71**(3), 251

The name given to reaction of a very electropositive metal with the oxide of a less active one, producing the less electropositive metal, usually incandescent. Archetypally a reaction between aluminium and iron oxide, now applied to a variety of similar combinations. Thermite reactions of rusty iron falling on other metals, especially magnesium protective electrodes, are a source of ignition of fires on oil tankers. Aluminium paint is only a danger if it has previously been to 150°C, the risk remains on cooling, bulk aluminium and alloys do spark fires, as can titanium [1]. The conditions under which incendive sparks are generated by impact of a striker with an aluminium smear on rusted steel were investigated. This was part of a comprehensive series of experiments to assess the importance of the variables and the mechanism of the process which leads to ignition of flammable materials in chemical plant environments [2]. Further to an earlier publication on the use of transition metal oxides in school demonstrations of thermite reactions [3], it was

stressed that use of manganese dioxide with aluminium may lead to explosion [4]. The use of potassium permanganate–glycerol mixture to ignite thermite mixture is more reliable than the magnesium ribbon/barium oxide:aluminium igniter [5].

Safety aspects are detailed for practical demonstrations of thermite reactions of aluminium with various oxides of chromium, cobalt, copper, iron, manganese, and nickel. The molar heat of reaction is maximal for Fe_3O_4, but the exotherm on a weight basis is maximal for the stoicheiometric mixture with MnO_2at 4.8 kJ/g [6]. The dependence of the burning rate on pressure (1–80 kbar) was studied for mixtures of magnesium, zinc or zirconium with barium dioxide, chromium(III) oxide, iron(III) oxide, manganese dioxide, molyybdenum trioxide, lead dioxide or vanadium pentoxide [7]. Combustion mechanisms for aluminium thermites with chromium(III) and Ni(II) oxides, also with silica, have been studied [12]. Five incidents in a survey of frictional ignition hazards probably involved thermite reactions [8], and the combustion rate of nickel oxide–aluminium mixtures is 2.5-fold greater than iron oxide mixtures [9]. Precautions necessary to activate large-scale (6 kg of mixture!) spectacular demonstrations are detailed [10]. Caution is given against conducting thermite demonstrations over water, or wet sand, after a lecture/demonstration audience were showered with hot iron [11]. A second-hand report of what is almost certainly the same incident claims that the front row of seats was pulverised–tales seldom lessen in the telling. Not only metal oxides but some halides undergo thermite type reactions with aluminium or magnesium [13]. Individually indexed examples are:

Aluminium, : Metal oxides, etc., 0048
Aluminium, : Sodium sulfate, 0048
Aluminium–magnesium alloy, : Iron(III) oxide, Water, 0053
Calcium acetylide, : Iron(III) chloride, Iron(III) oxide, 0585
Copper(I) oxide, : Aluminium, 4288
Iron(II,III) oxide, : Aluminium, Sulfur, 4405
Magnesium, : Metal oxides, 4690
Magnesium, : Metal oxosalts, 4690
Magnesium, : Rusty steel, 4690
Manganese(IV) oxide, : Aluminium, 4705

See other REDOX REACTIONS
See also VAPOUR EXPLOSIONS

DropBooks

THERMOCHEMISTRY AND EXOTHERMIC DECOMPOSITION

1. Grewer, T. *et al., Proc. 4th Symp. Loss Prev. Safety Prom. Proc. Ind.*, Vol. 3, A1–A11, Rugby, IChE, 1983
2. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986

The difficulties in relating the calculated thermodynamic energy of decomposition ($-\Delta U$) to that occurring in practice are discussed, and values of the experimentally observed energies of decomposition for some characteristic molecular structures are tabulated in comparison with the calculated values. A second table gives the range of decomposition energies which have been measured by DSC for

10 series of compounds each containing the same characteristic molecular structural group(s). These values are: — nitro, 220–410 kJ/mol (in 30 nitro compounds, with dinitro towards the top of the range); nitroso, 90–290 (4); oxime, 170–230 (2); isocyanate, 20–30 (3); azo, 100–180 (5); hydrazo, 65–80 (3); diazonium, 130–165 (5); peroxide, 200–340 (20); epoxide,4 5–80 (3); double bond, 40–90 (6). The reasons for the observed variation in these energies of decomposition are discussed.

The relationships between energy of decomposition and processing hazards are then considered, and the practical importance of using values of energy released per unit mass, rather than on a molar basis is stressed, and the decomposition energies in J/g are given in a further table. Finally it is suggested that in 'open vessel' processes (with man-hole sized opening), substances with exothermic decomposition energies below 500 J/g are not likely to be hazardous, but that in 'closed vessel' processes (opening is a safety valve or bursting disk), an upper limit of 150 J/g might be appropriate [1]. (Some of the alkali chlorate decomposition explosions experienced in, effectively open, bulk storage must have been of lower energy than 500 J/g — editor's comment.)

In a comprehensive investigation of exothermic decomposition, the thermal behaviour of a further 105 reactive componds (included below) in 18 classes was investigated by DSC, and the heats of decomposition so determined were tabulated. Of these compounds, 39, together with 21 other compounds, were investigated in detail in a series of adiabatic Dewar tests to examine the relationship between adiabatic temperature and induction time to exothermic decomposition. The adiabatic holding temperature which gives a time to exothermic decomposition of 24 hours has been proposed as a new practical characteristic for the particular compound. This temperature 'T_{ait24}' can be calculated from isothermal DTA diagrams [2], and this temperature is given in the text entries in this volume for the 60 compounds investigated.

Some other examples may be found in the entries:

Acetohydrazide, 0912
Acetone oxime, 1258
Acetylenedicarboxylic acid, 1405
† Acrylaldehyde, 1145
† Allyl acetate, 1912
N-Allylthiourea, 1600
4-Aminophenylazobenzene, 3487
Ammonium dichromate, 4246
Ammonium peroxodisulfate, 4576
4-Azidobenzaldehyde, 2697
2-Azido-2-phenylpropane, 3159
† Aziridine, 0863
Azobenzene, 3483
Azoformamide, 0816
Azoisobutyronitrile, 3011
Azoxybenzene, 3485
Benzaldehyde oxime, 2760

Benzyl chloride, 2738
4-Bromoaniline, 2296
2-Bromocyclohexanone, 2392
Butane-2,3-dione dioxime, 1595
† Butyl isocyanate, 1931
Chloroacetamide, 0788
4-Chloro-2-aminophenol, 2303
2-Chloroaniline, 2300
3-Chloroaniline, 2301
4-Chloroaniline, 2302
4-Chloro-1,2-benzenediamine, 2347
4-Chloro-1,3-benzenediamine, 2348
4-Chloro-2,6-diamino-*N* -methylaniline, 2822
1-Chloro-2,4-dinitrobenzene, 2098
† 1-Chloro-2,3-epoxypropane, 1162
3-Chloro-4-methoxyaniline, 2795
2-Chloronitrobenzene, 2141
4-Chloronitrobenzene, 2142
2(3-Chlorophenoxy)ethylamine, 2976
N-Chlorosuccinimide, 1427
N-Chlorotoluene-4-sulfonamide, 2797
Dibenzoyl peroxide, 3639
2,4-Dibromoaniline, 2226
2,3-Dichloroaniline, 2237
2,4-Dichloroaniline, 2238
2,5-Dichloroaniline, 2239
3,4-Dichloroaniline, 2241
N,N-Dichlorobenzenesulfonamide, 2244
2,4-Dimethoxyaniline, 2998
3,5-Dimethoxyaniline, 2999
Dimethyl acetylenedicarboxylate, 2340
N,N-Dimethyl-2-chloroacetamide, 1585
† 1,1-Dimethylhydrazine, 0954
N,N-Dimethyl-4-nitrosoaniline, 2980
† Dimethyl sulfoxide, 1588
2,4-Dinitroaniline, 2277
1,3-Dinitrobenzene, 2195
2,4-Dinitrophenol, 2197
3,5-Dinitro-2-toluamide, 2941
2,4-Dinitrotoluene, 2726
† 1,4-Dioxane, 1617
1,2-Diphenylhydrazine, 3517
1,1-Diphenylhydrazinium chloride, 3519
1,3-Diphenyltriazene, 3506
2,3-Epoxypropanol, 1229
† Ethylene oxide, 0829

DropBooks

Fumaric acid, 1446
Fumarodinitrile, 1397
Glucose, 2518
Glutarodinitrile, 1870
Hydroxylaminium sulfate, 4575
N-Hydroxysuccinimide, 1469
Maleic anhydride, 1404
Maleimide, 1418
Malononitrile, 1078
2-Methoxyaniline, 2816
3-Methoxyaniline, 2817
4-Methoxyaniline, 2818
3-Methoxybenzylamine, 2997
† 2-Methoxyethylamine, 1312
4-Methoxy-1,3-phenylenediamine, 2826
3-Methoxypropylamine, 1730
1-Naphthyl isocyanate, 3390
2-Nitroaniline, 2313
3-Nitroaniline, 2314
4-Nitroaniline, 2315
2-Nitrobenzaldehyde, 2686
3-Nitrobenzaldehyde, 2687
4-Nitrobenzaldehyde, 2688
Nitrobenzene, 2262
2-Nitrobenzoic acid, 2693
3-Nitrobenzoic acid, 2694
4-Nitrobenzoic acid, 2695
4-Nitrobenzyl chloride, 2714
4-Nitrodiphenyl ether, 3472
2-Nitrophenol, 2265
3-Nitrophenol, 2266
4-Nitrophenol, 2267
Nitrosobenzene, 2261
N-Nitrosodiphenylamine, 3486
1-Nitroso-2-naphthol, 3250
2-Nitrosophenol (1,2-Benzoquinone monoxime), 2263
4-Nitrosophenol (1,4-Benzoquinone monoxime), 2264
2-Nitrotoluene, 2763
4-Nitrotoluene, 2764
3-Phenoxy-1,2-epoxypropane, 3150
Phenyl azide, 2271
2-Phenylethyl isocyanate, 3139
Phenylhydrazine, 2373
Phenyl isocyanate, 2685
Poly(vinyl alcohol), 0831
Potassium hydrogen acetylenedicarboxylate, 1382

Potassium peroxodisulfate, 4668
† 2-Propen-1-ol, 1223
† Propylene oxide, 1225
Pyridine *N*-oxide, 1849
Sodium azide, 4758
Sodium chloroacetate, 0694
Sodium methoxide, 0464
Sodium 3-nitrobenzenesulfonate, 2184
Sodium peroxodisulfate, 4809
Sodium trichloroacetate, 0608
Styrene, 2945
Sucrose, 3558
1,2,4-Triazole, 0769
2,3,4-Trichloroaniline, 2163
Trimethylamine oxide, 1313
2,4,6-Trinitrotoluene, 2701

See also CELLULOSE

See CALORIMETRY, THERMAL STABILITY OF REACTION MIXTURES AND SYSTEMS

See also EXOTHERMICITY

THIOPHENOXIDES **ArS^-**

Diazonium salts

See DIAZONIUM SULFIDES AND DERIVATIVES (reference 9)

DropBooks

THORIUM FURNACE RESIDUES

Schmitt, C. R., *J. Fire Flamm.*, 1971, **2**, 163

Many furnace residues (fine powders and salts) deposited in the upper parts of furnaces used for thorium melting operations, are highly pyrophoric and often ignite as the furnace is opened. Such residues may be rendered safe by storage under water for 60–90 days. If the water is drained off early, ignition may occur.

See other PYROPHORIC MATERIALS

TOLLENS' REAGENT

1. Green, E., *Chem. & Ind.*, 1965, 943
2. Waldman, H., *Chimia*, 1959, **13**, 297–298
3. Coltoff, W., *Chem. Weekblad*, 1932, **29**, 737
4. MCA Guide, 1972, 319
5. Breedlove, C. H. *et al., J. Coll. Sci. Teach.*, 1983, **12**, 281
6. Klinger, G. S., *et al., Chem. Eng. News* 1996, **74**(2), 2

This mixture of ammoniacal silver oxide and sodium hydroxide solution is potentially dangerous, because if kept for a few hours it deposits an explosive precipitate. This danger was described by Tollens in 1882 but is not generally known now. Prepare the reagent just before use, in the tube to be used for the test, and discard

immediately after use, **NOT** into a container for silver residues [1]. Several earlier references to hazards of storing the reagent before or after use are discussed [2]. On one occasion a violent explosion of the reagent occurred 1 h after preparation and before a precipitate had formed [3], and on another, an empty but unrinsed test tube exploded when picked up [4]. Attempts to recover silver from a batch of the reagent of indeterminate age (!) caused explosions [5].

See FULMINATING METALS, SILVERING SOLUTIONS

TOXIC HAZARDS

While toxic hazards have been specifically excluded from consideration in this Handbook, such hazards are at least as important as reactive ones, and particularly on a long-term basis. Due account of toxic hazards must therefore be taken in planning and executing laboratory work, particularly if unfamiliar materials are being brought into use.

It is perhaps appropriate to point out that many of the elements or compounds listed in this Handbook are here because of a high degree of reactivity towards other materials. It may therefore broadly be anticipated that under suitable circumstances of contact with animal organisms (including readers), a high degree of interaction will ensue, with possible subsequent onset of toxic or other deleterious effects.

See APROTIC SOLVENTS

TRIALKYLALUMINIUMS R_3Al

Basyrov, Z. B. *et al., Chem. Abs.*, 1988, **109**, 215294

In a review of the fire and explosibility hazards of this group, data on 15–50% solutions of trimethyl- and triisobutyl-aluminium in isopentane and in hexane are given.

A highly reactive group of compounds, of which the lower members are extremely pyrophoric, with very short ignition delays of use in rocket- or jet-fuel ignition systems. Storage stability is generally high (decomposition with alkene and hydrogen evolution begins above about 170–180°C), but branched alkylaluminiums (notably triisobutylaluminium) decompose above 50°C. Individually indexed compounds, many commercially available in bulk, are:

3-Buten-1-ynyldiethylaluminium, 3017
3-Buten-1-ynyldiisobutylaluminium, 3549
∗ Diethyl-3-diethylaminopropylaluminium, 3414
† Triethylaluminium, 2553
† Triisobutylaluminium, 3568
Triisopropylaluminium, 3214
Trimethylaluminium, 1291
Tripropylaluminium, 3215
∗ Tris(trimethylsilylmethyl)aluminium, 3584
∗ Tris(trimethylsilylmethyl)indium, 3585

TRIALKYLANTIMONY HALIDES R_3SbX

Leleu, *Cahiers*, 1977, (88), 361

These ignite spontaneously in air.
See other ALKYLMETAL HALIDES

TRIALKYLBISMUTHS **R_3Bi**

Oxidants
Gilman, H. *et al.*, *Chem. Rev.*, 1942, **30**, 291
The lower alkylbismuths ignite in air, and explode in contact with oxygen, or conc. nitric or sulfuric acids. Individually indexed compounds are:
Tributylbismuth, 3571
Triethylbismuth, 2561
∗ Trivinylbismuth, 2391
See other ALKYLMETALS

TRIALKYLSILYLOXY ORGANOLEAD DERIVATIVES **$R_3SiOPbR'_3$**

Houben-Weyl, 1975, Vol. 13.7, 118
Compounds containing Si−O−Pb bonds may interact explosively with oxygen at about 140°C, or with aluminium chlorides, acyl halides or anhydrides.
See related ALKYLMETALS, ALKYLNON-METALS

TRIAZENES **$RN{=}N{-}NR'R''$**

1. Houben Weyl, 1967, 10/2, 827
2. Houben-Weyl, 1965, Vol. 10.3, 700, 717, 722, 731
3. Vaughan, K. *et al.*, *Chem. Soc. Rev.*, 1978, **7**, 378–379
4. White, E. H. *et al.*, *Org. Synth.*, 1973, Coll. Vol. 5, 797
5. Rondevstedt, C. S. *et al.*, *J. Org. Chem.*, 1957, **22**, 200

DropBooks

Care is required with these compounds since many explode on heating [1]. A number of triazene derivatives bearing hydrogen, or cyano, hydroxy or nitroso groups on the terminal nitrogen of the chain are unstable, mainly to heat [2]. Purification of triazenes by vacuum sublimation carries the risk of explosion [3]. Further examples of unstable triazenes and precautions are given [4,5].
Individually indexed compounds are:
∗ 1-Acetyl-4-(4′-sulfophenyl)-3-tetrazene, 2982
1-Benzyl-3-(4-tolyl)triazene, 3657
1,3-Bis(phenyltriazeno)benzene, 3757
Copper(II) 1,3-di(5-tetrazolyl)triazenide, 1429
3,3-Dimethyl-1-phenyltriazene, 2996
3,3-Dimethyl-1-(3-quinolyl)triazene, 3398
1,3-Dimethyltriazene, 0945
∗ 1,5-Diphenylpentaazadiene, 3507
1,3-Diphenyltriazene, 3506
1,3-Di(5-tetrazolyl)triazene, 0778
3-Ethyl-1(4-methylphenyl)triazene, 3171
1-(4-Methoxyphenyl)-3-methyltriazene, 3000
1-(2-Naphthyl)-3-(5-tetrazolyl)triazene, 3394
N-Phenylazopiperidine, 3407

1-Phenyl-3-*tert*-butyltriazene, 3335
Silver 3-cyano-1-phenyltriazen-3-ide, 2670
Silver 1,3-di(5-tetrazolyl)triazenide, 0690
See 3-CYANOTRIAZENES
3-HYDROXYTRIAZENES
3-NITROSOTRIAZENES
See other HIGH-NITROGEN COMPOUNDS

TRIAZOLES

1. Wilson, W. S. *et al., Austr. J. Chem.*, 1992, **45**(3), 513, 525
2. Grimmett, M. R.; *Barton & Ollis*, 1979, Vol. 4, 364

For a study of nitrophenylbenzotriazoles as explosives, the triazole ring conferring impact sensitivity, see [1]. Simpler nitro- and azido-triazoles also find explosive use. On heating to above 260°C, 1,2,3-triazole halides explode violently [2]. Several examples of instability among this group of relatively high-nitrogen compounds may be found under the entries:

4-Amino-4*H*-1,2,4-triazole, 0812
5-Amino-3-phenyl-1,2,4-triazole, 2952
Ammonium 3,5-dinitro-1,2,4-triazolide, 0823
3-Azido-1,2,4-triazole, 0717
3,3′-Azo-(1-nitro-1,2,4-triazole), 1401
Benzotriazole, 2269
1,3-Bis(5-amino-1,3,4-triazol-2-yl)triazene, 1576
Bis(1-benzo[*d*]triazolyl) carbonate, 3598
Bis(1-benzo[*d*]triazolyl) oxalate, 3629
∗ Bis(1-methylbenzotriazole)cobalt(II) nitrate, 3652
N-Chloro-4,5-dimethyltriazole, 1490
5-Cyano-4-diazo-4*H*-1,2,3-triazole, 1345
4-Diazo-5-phenyl-1,2,3-triazole, 2910
3-Diazo-5-phenyl-3*H*-1,2,4-triazole, 2909
4-Diazo-1,2,3-triazole, 0678
3-Diazo-3*H*-1,2,4-triazole, 0677
4,6- or 5,6- or 5,7-Dinitro-1-picrylbenzotriazoles, 3439
Ethyl 4-diazo-1,2,3-triazole-5-carboxylate, 1853
∗ 5-Hydrazino-1,2,3,4-thiatriazole, 0462
1-Hydroxybenzotriazole, 2272
4-Hydroxy-3,5-dimethyl-1,2,4-triazole, 1575
1-Hydroxy-2-hydroxylamino-1,3,4-triazole, 0817
∗ 5-Methoxy-1,2,3,4-thiatriazole, 0773
1-Methyl-1,2,3-triazole, 1189
4-Nitroamino-1,2,4-triazole, 0777
4-Nitro-1-picryl-1,2,3-triazole, 2886
3-Nitro-1,2,4-triazolone, 0716
1-Picryl-1,2,3-triazole, 2893
Silver benzo-1,2,3-triazole-1-oxide, 2127

1,2,3-Triazole, 0768
1,2,4-Triazole, 0769
1,2,4-Triazole-3-diazonium nitrate, 0680
See other HIGH-NITROGEN COMPOUNDS

TRICARBONYL(CYCLOPENTADIENYL)SILYLMETAL COMPLEXES

Hagen, A. P. *et al., Inorg. Synth.*, 1972, **17**, 104
During the preparation of the complexes of chromium, molybdenum and tungsten from $K[M(CO)_3C_5H_5]$ and bromosilane, the residues from sublimation of the products are all pyrophoric.
See related CARBONYLMETALS, ORGANOMETALLICS

***N,N,N″*-TRIFLUOROAMIDINES** **$-C(NF)NF_2$**

Ross, D. L. *et al., J. Org. Chem.*, 1970, **35**, 3093
This group of compounds, (which combines the structural features of both the separately treated *N*-HALOIMIDES and DIFLUOROAMINO COMPOUNDS, each of high reactivity) is explosively unstable.

All the N−F compounds involved in the synthesis of a group of C_3-C_7N-trifluoroalkylamidines were shock-sensitive explosives in varying degrees. Several were only stable in solution, and others exploded during analytical combustion. Individually indexed compounds are:
2-Chloro-*N,N,N′*-trifluoropropionamidine, 1128
Decafluorobutyramidine, 1371
∗ Pentafluoroguanidine, 0359
Perfluoro-1-aminomethylguanidine, 0647
Perfluoroformamidine, 0350
N,N,N′-Trifluorohexanamidine, 2448
N,N,N′-Trifluoropropionamidine, 1172
See other *N*-HALOGEN COMPOUNDS

DropBooks

TRINITROETHYL ORTHOESTERS **$HC[OCH_2C(NO_2)_3]_3$, $C[OCH_2(NO_2)_3]_4$**

Nitromethane
Shimio, K. *et al., Chem. Abs.*, 1976, **85**, 194924
Both tris(2,2,2-trinitroethyl)orthoformate and tetrakis(2,2,2-trinitroethyl)-orthocarbonate form powerfully explosive solutions in nitromethane. The oxygen balance of the esters are +154 and +182%, respectively. The compounds are:
Tetrakis(2,2,2-trinitroethyl)orthocarbonate, 3132
Tris(2,2,2-trinitroethyl) orthoformate, 2786
See OXYGEN BALANCE, POLYNITROALKYL COMPOUNDS

TURPENTINE

NSC 367, 1968;
HCS 1980, 948

Paulin, M. S., *Tappi J.*, 1983, **66**(4), 91−92

A 45 kl tank of sulfate turpentine from a paper mill became dangerously heated, owing to oxidation arising from local high temperature and an air-purging procedure.

Diatomaceous earth

Anon., *Ind. Eng. Chem.*, 1950, **42**(7), 77A

A large quantity of discoloured (and peroxidised) turpentine was heated with fuller's earth to decolourise it, and it subsequently exploded. Fuller's earth causes exothermic catalytic decomposition of peroxides and rearrangement of the terpene molecule.

Halogens, or Oxidants, or Tin(IV) chloride

Mellor, 1941, Vol. 2, 11, 90; 1941, Vol. 7, 446; 1943, Vol. 11, 395

Turpentine ignites in contact with fluorine (at −210°C), chlorine, iodine, chromium trioxide, and chromyl chloride, and usually with tin(IV) chloride. Other highly unsaturated hydrocarbons may be expected to react similarly.

Other reactants

Yoshida, 1980, 290

MRH values calculated for 13 combinations with oxidants are given.

See Calcium hypochlorite: Turpentine

Nitric acid: Hydrocarbons (reference 16) MRH 6.03/82

UNIT PROCESS OR UNIT OPERATION INCIDENTS

1. Shabica, A. C., *Chem. Eng. Progr.*, 1963, **59**(9), 57–66
2. *Organic chemical manufacturing hazards*, Goldfarb, A. S. et al., Zurich, Technomic Publishing, 1981
3. *Control of industrial chemical hazards*, Carson, P. A. et al., Harlow UK, Longmans, (2 Vols) 1989
4. *Hazards of commercial chemical reactions; Hazards of commercial chemical operations*, Austin, G. T., Chs. 4, 5 in *Safety and accident prevention in chemical operations*, Fawcett, H. H. and Wood, W. S. (eds), New York, Wiley, 2nd edn., 1982

In a paper on the qualitative evaluation of hazards in organic batch chemical processing operations, the following types of reaction are rated for hazard on a scale of A–E. Reduction (13 methods); oxidation (13 methods); alkylation, C–C (13 methods), C–O (5 methods), C–N (5 methods); condensation (16 methods); amination (3 methods); esterification (9 methods); hydrolysis; substitution; peroxide preparations (2 methods); pyrolysis (2 methods); Schmidt reation; Mannich reaction; halogenation (3 methods); nitration (2 methods). Some 200 common reagents and solvents are also hazard-rated, and general precautions and techniques to avoid batch processing hazards are listed [1]. Three more recent texts deal with the hazards of specific industrial processes or groups of products [2,3], or with unit processes or operations [4].

Incidents have been grouped for each of the unit process or unit operation headings:

AGITATION INCIDENTS, AMINATION INCIDENTS, CATALYTIC NITRO REDUCTION PROCESSES

DIAZOTISATION, DRYING, EPOXIDATION, GAS EVOLUTION INCIDENTS
GRIGNARD REAGENTS, HALOGENATION INCIDENTS, HYDROGENATION INCIDENTS
IRRADIATION DECOMPOSITION INCIDENTS, MIXING, NEUTRALISATION INCIDENTS, NITRATION INCIDENTS
OXIDATION INCIDENTS, PEROXIDATION INCIDENTS, PLANT CLEANING INCIDENTS
POLYCONDENSATION REACTION INCIDENTS, POLYMERISATION INCIDENTS, REDOX REACTIONS, SULFONATION INCIDENTS

UNSATURATED OILS

See Linseed oil
Carbon: Unsaturated oils, 0298

URANYL MACROCYCLIC PERCHLORATE LIGANDS

Vidali, M. *et al.*, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1715–1719
A series of uranyl complexes of macrocyclic azomethines were used as ligands for transition metal ions, with perchlorate anions. Raman spectra of the uranyl–metal complexes could not be recorded because the samples exploded during attempted measurements.
See other AMMINEMETAL OXOSALTS, IRRADIATION DECOMPOSITION INCIDENTS

DropBooks

VACUUM DISTILLATION RESIDUES

1. Editor's comments, 1995
2. Cardillo, P. *et al.*, *Chem. Abs.*, 1998, **128**, 118814h

Explosions shortly after the completion of vacuum distillations are common. There are two causes, firstly that the residues are unstable and, heat removal declining with the cessation of agitation and evaporation, there is unaided thermal runaway from the elevated temperature at which such distillations commonly finish. The second is that the still very hot vessel has been repressurised with air, and residues are usually combustible. Cooling of such residues should be checked, if not assisted, and air not admitted to the vessel until it is below 100°C [1]. An account of the investigation of an industrial accident of the first type is available [2].
Some examples: 4-Chloro-2-methylaniline 2-Chloro-4-nitrotoluene: Sodium hydroxide 2-Nitrobenzaldehyde (reference 4) 4-Nitrophenylacetic acid: Acetic anhydride, Pyridine 4-Nitrotoluene (reference 3)
See also COOL FLAMES

VACUUM PUMPS

1. Ripper, L. J., *Vak. Praxis*, 1994, **6**(2), 91; *Chem. Abs.*, 1995, **122**, 87800v
2. Oliver, G., *Chemical Engineer*, 1996, (619), s21
3. Grabs, E., *PTB-Mitt.*, 1996, **106**(5), 345

Some reviews on explosion prevention measures for vacuum pumps have been published, including consideration of possible sources of ignition [1]. The second is a discussion of how to prevent and contain explosions in the various cavities of dry vacuum pumps where fuel/oxygen mixes may be present. In view of the ability of oil pumps to generate mists, they may be an even greater danger than dry ones [2]. Another review of vac. pumps pumping potentially explosive mixtures, e.g. in fuel recovery at filling stations, has been written [3].

See Oxygen: Plastic tubes

VAPOUR CLOUD EXPLOSIONS

1. van Wingerden, C. J. M. *et al., Plant/Oper. Progr.*, 1989, **8**(4), 234
2. Johnson, D. M. *et al., Hazards XI*, 67, Symp. Ser. **124**, Rugby (UK), IChE, 1991
3. Abou Arab, *et al., J. Loss Prev. Process Ind.*, 1991, **4**(3), 202
4. Mercx, W. P. M., *Trans. Inst. Chem. Eng.*, 1992, **70** (B4), 197
5. Anon., *Loss Prev. Bull.*, 1991, **099**
6. Davenport, J. A. *et al., Process Safety Progr.*, 1993, **12**(1), 12
7. Mancini, R. A., *Plant/Oper. Progr.*, 1992, **11**(1), 27; Bull, D. C., *ibid.*, 33
8. Mercx, W. P. M. *et al., Process Safety Progr.*, 1993, **12**(4), 222
9. Mercx, W. P. M. *et al., Process Safety Progr.*, 1995, *14*(2), 121
10. Bjerketvedt, D. *et al., J. Hazard Mat.*, 1997, **52**(1), 1

This term (or, confusingly, Vapour Explosion) is used for releases of superheated flammable liquids, or gases, followed by ignition after a delay, which may be of some minutes. Overpressures are slight and deflagration slow in open, unobstructed spaces. Obstruction and partial confinement accelerate the flame front and produce blasts such as Flixborough; a predictive model is described and demonstrated on Flixborough, understanding is not yet complete [1]. There may be substantial delay between ignition and significant overpressure. Experiments and their results with large-scale natural gas release are described [2]. Smaller scale experiment is described [3]. A comparison of large scale experiments with small (even these of several m^3) is given; high energy fuels, especially ethene, show transition to detonation in obstructed spaces [4]. The most damaging industrial explosions of the last few decades have been of this nature [5,6]. For reviews of both the theory and experiment: [7]. The development of methods to predict the blast risks is described [8]. Techniques for experimental vapour cloud explosion studies are evaluated [9]. A handbook on (natural) gas explosion safety has been published [10].

See also BLEVE, GEOMETRY OF VESSELS AND PIPEWORK, DEFLAGRATION TO DETONATION

VAPOUR EXPLOSIONS

1. Fröhlich, G., *Chem. Ing. Tech.*, 1978, **50**, 861–866
2. Ogiso, C. *et al., Chem. Abs.*, 1985, **102**, 190161
3. Iida, Y. *et al., JSME Int. J.*, 1987, **30**, 1972–1981

4. Fletcher, D. F. *et al., J. Loss Prev.*, 1994, **7**(6), 457
5. Theofanous, T. G. *et al, Phys. Fluids*, 1994, **6**(11), 3513

A vapour explosion can occur on contact between 2 liquids of differing temperatures if the temperature of the hotter liquid is above the b.p. of the cooler, and the explosion is due to extremely rapid vapour generation (phase transition) of the cooler liquid. Vapour generation must be preceeded by very good heat transfer by a fragmentation process leading to enormous heat transfer coefficients. Experimental results are discussed for water as the cooler liquid and melts of glass, aluminium, copper, iron, gallium or lead as the hotter liquid. The probability of steam explosions depends on the materials of the melt, the temperatures of the 2 liquids (not only the temperature difference), the reacting masses, the shape of the container and external triggering (by impact, etc.) [1]. An experimental study of vapour explosions of water in contact with sodium carbonate–sodium chloride hot melts is reported[2]. The mechanism of vapour explosions caused by drops of molten lithium nitrate falling into ethanol has been studied by high-speed photography and pressure trace measurements [3]. Recent work in the area is reviewed, with a description of the processes involved. It is suggested that the Krakatoa eruption was the largest incident on record [4]. Interaction of molten aluminium and water is studied, in particular the conditions in which vapour explosion can initiate chemical reaction [5].

See LIQUEFIED GASES, MOLTEN METAL EXPLOSIONS, SMELT, SUPERHEATED LIQUIDS

VEGETABLE OILS

DropBooks

Catalysts, Hydrogen

See Hydrogen: Catalysts, Vegetable oils

VINYLSILOXANES

Schilling, C. L., *et al., Chem. Eng. News*, 1994, **72**(37), 2

Vinyl siloxanes are prone to uncontrolled exotherm and explosion without other than thermal assistance. There is extremely rapid pressure generation in closed containers from about 200°C.

See SILANES

VINYL SULFOXIDES C=C.SO$_2$–

Nikonov, V. A. *et al., Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**(7,1), 1374; *Chem. Abs.* 1990, **112**, 29847

Complexes of butyl vinyl sulfoxide and iron, chromium and cobalt (III) nitrates were found to be unstable, the ferric salt (the least stable) exploding even as a 40 mol% solution in benzene. It is considered that other vinyl sulfoxide ligands will behave similarly.

See METAL NITRATES

VIOLENT POLYMERISATION

1. Harmon, M. *et al.*, *A Review of Violent Monomer Polymerisation*, Rept. AD-017443, Richmond (Va.), USNTIS, 1974
2. Bond, J., *Loss Prev. Bull.*, 1985 (065), 21–28
3. Frurip, D. J. *et al.*, *Process Safety Progr.*, 1995, **14**(2), 79
4. Ogiso, C. *et al.*, *Chem. Abs.*, 1986, **105**, 29100
5. Encyclop. Polym. Sci. Eng., Mark, H. F. *et al.* (eds), Vol. 14, 805–827, New York, Wiley, 1988
6. Thomas, I. F. in *Integrated Risk Management* (Eds: Melchers & Stewart), 177, Rotterdam, Balkema,1995

Radical polymerisations, in particular, are liable to run out of control. There are three reasons for this; firstly monomers may contain traces of inhibitors, in which case the rate of polymerisation will rise when these are exhausted, secondly the physics of polymer solution cause the termination rate of radical chains to decline as the reaction proceeds, meaning acceleration and increased heat evolution exactly when increasing viscosity makes it difficult to remove (the Norrish–Tromsdorff effect). The third possibility is 'popcorn polymerisation' (so called from the appearance of the product) which is a spontaneous event, usually during storage, in which polymer gel particles are thought to be osmotically swollen by penetrating monomer to the degree of rupturing bonds: more radicals and, effectively, a branched chain process.

Literature related to the possibility of violent polymerisation of the 10 monomers most significant industrially has been classified and reviewed, and 209 annotated references are given. The compounds covered are acrylic acid, acrylonitrile, 1,3-butadiene, ethylene, ethylene oxide, methyl acrylate, methyl methacrylate, propiolactone, styrene, vinyl acetate, vinyl chloride and vinylidene chloride. Almost all have been involved in explosive polymerisation incidents. For each compound, data and selected references on physical properties, reactivity, inhibition and handling procedures are given [1]. Mechanisms of initiation, inhibition, and de-inhibition of polymerisation are reviewed briefly, with 8 case histories of incidents involving violent polymerisation of 6 common monomers [2]. A procedure is given for assessing monomers for risk of runaway polymerisation [3]. Conditions for runaway reactions in suspension polymerisation when stirring is stopped were determined experimentally. A vapour explosion was observed in a closed system under runaway conditions [4]. A 22-page section devoted to safety aspects of the production and uses of polymeric materials covers a wide range of relevant topics in polymerisation and processing plant management, including a comprehensive reference list [5].

Acrylic monomers, in particular, are inclined to polymerisation in the absence of oxygen which serves as a chain-breaker in their radical polymerisation. Most such monomers are also flammable and may therefore be directed to be stored under a nitrogen blanket. If nitrogen purging is complete, the risk of fire within vessels may be zero, but the risk of explosive polymerisation, tank-rupture and external fire is increased. Some suspect that accidents of this type have occurred already [6].

Detailed examples may be found in the entries:
† Acrylonitrile, : Initiators, 1107
† 1,2-Butadiene, 1479
† 1,3-Butadiene, 1480
† 1,1-Dichloroethylene, 0695
† Ethylene, 0781
† Ethylene oxide, : Ammonia, 0829
† Methyl acrylate, 1531
See ACRYLIC MONOMERS
See also POLYMERISATION INCIDENTS

WASTE DISPOSAL

See DISPOSAL

WATER-REACTIVE COMPOUNDS

A large number of individual compounds react exothermally and violently with water, particularly with restricted amounts of the latter. Many such compounds come within the groups:

ACID ANHYDRIDES, ACYL HALIDES, ALKALI METALS
ALKYLALUMINIUM DERIVATIVES, ALKYLNON-METAL HALIDES
COMPLEX HYDRIDES, METAL HALIDES, METAL HYDRIDES
METAL OXIDES, NON-METAL HALIDES (AND THEIR OXIDES)
NON-METAL OXIDES

DropBooks

WAX FIRE

Carbon tetrachloride
1. Gilmont, R., *Chem. Eng. News*, 1947, **25**, 2853
2. Author's comment, 1989

Use of carbon tetrachloride to extinguish a wax fire caused an explosion. This was attributed to a violent reaction between unsaturated wax components and carbon tetrachloride initiated by radicals from decomposing peroxides [1]. Perhaps a more likely explanation could be that contact of the cold low-boiling liquid with the hot molten wax led to the physical effect of a vapour explosion, rather than the chemical explosion postulated [2].
See Dibenzoyl peroxide: Carbon tetrachloride

WOOD PULP

Eidsan, G. *et al.*, *Biotechnol. Lett.*, 1979, **1**, 31–34

Semi-chemical pulp contaminated with micro-organisms and incubated at 60°C produces a hydrogen-containing gas. A gas-phase explosion in a pulp storage tower was attributed to static ignition of this gas admixed with air.
See other STATIC INITIATION INCIDENTS

WOOL

Lee, P. R., *J. Appl. Chem.*, 1969, **19**, 345–351

The self-heating and ignition of baled or loose wool in bulk storage is discussed and analysed, and steady state thermal explosion theory is applied to the prediction of critical masses and induction periods for storage and transportation situations in relation to ambient temperature. Results obtained were consistent with current safety practices.

WORKERS AT THE NEXT BENCH

Are almost as dangerous as are you, dear reader. Make sure you know what he is doing and expect her to return the compliment.

'XANTHATES' **ROC(S)S$^-$**

1. Sorbe, 1968, 74
2. Anon., Private communication, 1990
3. Kirk-Othmer, 1984, 3rd Edn., Vol. 24, 646

Salts of *O*-alkyldithiocarbonates ('xanthates') are hazardous as dusts, forming explosive suspensions in air. The lower-alkyl salts are claimed to be explosive in the solid state when dry [1]. Explosions reported when drying hydrated xanthate salts are probably the consequence of release of carbon disulphide to form an inflammable atmosphere of very low autoignition temperature in the oven [2]. Xanthate esters are thermally unstable by a variety of eliminations and rearrangements, all distinctly exothermic and many evolving extremely flammable gases and vapours. Free xanthic acids, which may be isolated on acidification, decompose autocatalytically and perhaps explosively [3].

See Potassium *O*-ethyl dithiocarbonate

See also Carbon disulfide

Diazonium salts

See DIAZONIUM SULFIDES AND DERIVATIVES (reference 8)

XENON COMPOUNDS **Xe–F, Xe–O**

1. Jha, N. K., *RIC Rev.*, 1971, **4**, 16765168
2. Kirk-Othmer, 3rd Edn., 1980, Vol. 12, 293; 4th Edn, 1995, Vol. 13, 9

For convenience, the even rarer and less stable krypton compounds are also covered in this entry. All xenon compounds are very strong oxidants and many are also explosively unstable. For a now obsolete review, see [1]. A recent compact review of noble gas chemistry is found in [2]. A series of alkali xenates, $MHOXeO_3.1.5H_2O$ are unstable explosive solids. The equivalent fluoroxenates $MFXeO_3$are far more stable. Individually indexed compounds are:

Caesium bromoxenate, 0237

Caesium chloroxenate, 3970

Caesium hydrogen xenate, 4259

∗ Krypton difluoride, 4313
Potassium hexaoxoxenonate−xenon trioxide, 4674
Tetrafluoroammonium hexafluoroxenate, 4386
Xenon difluoride dioxide, 4322
Xenon difluoride oxide, 4319
Xenon difluoride, 4332
Xenon hexafluoride, 4377
Xenon tetrafluoride, 4353
Xenon tetrafluoride oxide, 4346
Xenon tetraoxide, 4863
Xenon trioxide, 4857
Xenon(II) fluoride methanesulfonate, 0443
Xenon(II) fluoride perchlorate, 3977
Xenon(II) fluoride trifluoroacetate, 0634
Xenon(II) fluoride trifluoromethanesulfonate, 0356
Xenon(IV) hydroxide, 4533
Xenon(II) pentafluoroorthoselenate, 4382
Xenon(II) pentafluoroorthotellurate, 4383
Xenon(II) perchlorate, 4110

See other NON-METAL HALIDES, NON-METAL OXIDES

YEAST

1. Anon., *The Daily Telegraph* (London), Jan. 30th 1996, 6
2. Editor's comments

A package of brewers' yeast exploded, slightly injuring three postal workers [1]. Fermentations in sealed containers can easily generate sufficient pressure of carbon dioxide to rupture the container. The problem is well known to home ginger beer makers and Champagne houses; now that yeast is sometimes used as a reducing agent it is appearing in the chemical world [2].

See SUGARS

DropBooks

ZINC BACITRACIN

Piotrowski, T., *Chem. Abs.*, 1984, **101**, 60040

In a study of explosive potential of 20 pharmaceutical products, zinc bacitracin was identified as unusual, in that though not normally explosive, when it does explode it produces relatively high pressures.

See entry PRESSURE INCREASE IN EXOTHERMIC DECOMPOSITION

Appendix 1

Source Title Abbreviations used in Handbook References

The abbreviations used in the references for titles of journals and periodicals are those used in BP publications practice and conform closely to the recommendations of the *Chemical Abstracts* system. Abbreviations which have been used to indicate textbook and reference book sources of information are set out below with the full titles and publication details.

ABCM Quart. Safety Summ.,	*Quarterly Safety Summaries*, London, Association of British Chemical Manufacturers, 1930–1964
ACS 54, 1966	*Advanced Propellant Chemistry*, ACS 54, Washington, American Chemical Society, 1966
ACS 88, 1969	*Propellants Manufacture, Hazards and Testing*, ACS 88, Washington, American Chemical Society, 1969
Albright, Hanson, 1976	*Industrial and Laboratory Nitrations*, ACS Symposium Series 22, Albright, L. F., Hanson, C., (Eds.), Washington, American Chemical Society, 1976
Alkali Metals, 1957	*Alkali Metals*, ACS 19, Washington, American Chemical Society, 1957
ASHRAE. J.	*American Society of Heating, Refrigeration and Air-conditioning Engineers Journal*, New York.
Augustine, 1968	*Reduction, Techniques and Applications in Organic Chemistry*, Augustine, R. L., London, Edward Arnold, 1968

Augustine, 1969, 1971 — *Oxidation, Techniques and Applications in Organic Synthesis*, Augustine, R. L., (Ed.), New York, Marcel Dekker, Vol. 1, 1968, Vol. 2 (with Trecker, D. J.), 1971

Bahme, 1972 — *Fire Officer's Guide to Dangerous Chemicals*, FSP-36, Bahme, C. W., Boston, National Fire Protection Association, 1972

Bailar, 1973 — *Comprehensive Inorganic Chemistry*, Bailar, J. C., Emeléus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., (Eds.), Oxford, Pergamon, 5 vols., 1973

BCISC Quart. Safety Summ., — *Quarterly Safety Summaries*, London, British Chemical Industries Safety Council, 1965–1973

Barton & Ollis, 1979 — *Comprehensive Organic Chemistry*, Barton, D. H. R.,Ollis, W. D., (Eds), Oxford, Pergamon, 1979.

Biasutti, 1981 — *History of Accidents in the Explosives Industry*, Biasutti, G. S. (Author and publisher), Vevey, 1981

Bond, 1991 — *Sources of Ignition*, Bond, J., Oxford, Butterworth-Heinemann, 1991

Braker, 1981 — *Matheson Gas Data Book*, Braker, W., Mossman, A. L., Lyndhurst (NJ), Matheson Div. Searle, 6th edn. 1981

Brandsma, 1971 — *Preparative Acetylenic Chemistry*, Brandsma, L., Barking, Elsevier, 1971

Brauer, 1961, 1965 — *Handbook of Preparative Inorganic Chemistry*, Brauer, G., (Translation Ed. Riley, R. F.), London, Academic Press, 2nd edn. Vol. 1, 1963; Vol. 2, 1965

Bretherick, 1986 — *Hazards in the Chemical Laboratory*, Bretherick, L. (Ed.), London, Royal Society of Chemistry, 4th edn., 1986

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Castrantas, 1970 — *Laboratory Handling and Storage of Peroxy Compounds*, Special Publication No. 491, Castrantas, H. M., Banerjee, D. K., Philadelphia, ASTM, 1970

DropBooks

CHAS Notes	*Chemical Health and Safety Notes*, ACS Division of Chemical Health and Safety, Washington, 1982 to date (4 issues/yr)
Chemiarbeit	*Chemiearbeit, Schutzen und Helfen*, Dusseldorf, Berufsgenossenschaft der Chemische Industrie, 1949–1962 (supplement to Chemische Industrie)
Chem. Hazards Ind.	*Chemical Hazards in Industry*, Royal Society of Chemistry Information Group, Cambridge, 1984 to date (monthly abstracts)
CISHC Chem. Safety Summ.,	*Chemical Safety Summaries*, London, Chemical Industry Safety and Health Council of the Chemical Industries Association, 1974 to 1986 (terminated)
CHETAH 1990	*The ASTM Chemical Thermodynamic and Energy Release Evaluation Programme*, Version 4.4, 2nd Edn (ASTM Data Series Publication 51A), Davies C. A. *et al*., Philadelphia, ASTM, Appendix V. Upgrades continue to be issued (1998)
Cloyd, 1965	*Handling Hazardous Materials*, Technical Survey No. SP-5032, Cloyd, D. R., Murphy, W. J., Washington, NASA, 1965
Coates, 1960	*Organometallic Compounds*, Coates, G. E., London, Methuen, 1960
Coates, 1967, 1968	*Organometallic Compounds*, Coates, G. E., Green, M. L. H., Wade, K., London, Methuen, Vol. 1, 1967, Vol. 2, 1968
Compendium 1985, 1987	*Compendium of Safety Data Sheets, for Research and Industrial Chemicals*, Keith, L. H., Walters, D. B., Deerfield Beach/Weinheim, VCH, vols. 1–3 of 867 sheets 1985, vols 4–6 of 723 sheets, 1987
Dangerous Loads, 1972	*Dangerous Loads*, Leicester, Institution of Fire Engineers, 1972
Dangerous Substances, 1972	*Dangerous Substances: Guidance on Fires and Spillages* (Section 1, 'Inflammable liquids'), London, HMSO, 1972
Davies, 1961	*Organic Peroxides*, Davies, A. G., London, Butterworths, 1961
Davis, 1943	*Chemistry of Powder and Explosives*, Davis, T. L., New York, Wiley, 1943

DOC 5, 1982 — *Dictionary of Organic Compounds*, Buckingham, J., (Ed.), London, Chapman & Hall, 5th edn. in 5 vols. + indices, 1982, annual supplementary vols. to date

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Federoff, 1960 — *Encyclopaedia of Explosives and Related Compounds*, Federoff, B. T. (Ed.), Dover (NJ), Piccatinny Arsenal, Vol. 1, 1960; Vol. 10, 1984 (from USNTIS)

Fieser, 1967–1986 — *Reagents for Organic Synthesis*, Fieser, L. F. and Fieser, M., New York, Wiley, Vol. 1, 1967, The series continues after the death of the originator.

Freifelder, 1971 — *Practical Catalytic Hydrogenation*, Freifelder, M., New York, Wiley-Interscience, 1971

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Goehring, 1957 — *Ergebnisse und Probleme der Chemie der Schwefelstickstoff-verbindung, Scientia Chemica*, Vol. 9, Goehring, M., Berlin, Akademie Verlag, 1957

Grignard, 1935–54 — *Traité de Chimie Organique*, Grignard, V. and various volume Eds., Paris, Masson, Vol. 1, 1935, Vol. 23, 1954

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Guide for Safety, 1972 — *Guide for Safety in the Chemical Laboratory*, MCA, New York, Van Nostrand Reinhold, 2nd edn., 1972

Harmon, 1974 — *A Review of Violent Monomer Polymerisation*, Harmon, M., King, J., Rept. AD-017443, Springfield (Va.), NTIS, 1974

Haz. Chem. Data, 1975 — *Hazardous Chemical Data*, NFPA 49, Boston, National Fire Protection Association, 1975

HCS 1980 — *Handling Chemicals Safely*, Dutch Assoc. of Safety Experts, Dutch Chemical Industry Assoc., Dutch Safety Inst., 1980 (Engl. transl. of 2nd Dutch edn.)

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Kit and Evered, 1960	*Rocket Propellant Handbook*, Kit, B., Evered, D. S., London, MacMillan, 1960
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Leleu, Cahiers, 1972–80	*Les Réactions Chimique Dangereuse*, Leleu, J., published serially in *Cahiers de Notes Documentaires*, from 1972 **(68)**, 319 to 1980, **(100)**, 426
Loss Prev. Bull., 1974 to date	*Loss Prevention Bulletin*, Rugby, Institution of Chemical Engineers, 6 issues annually since 1974
Mackay, 1966	*Hydrogen Compounds of the Metallic Elements*, Mackay, K. M., London, Spon, 1966
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(MCA SD-Series) 1947–76	*Safety Data Sheets*, MCA, Washington. The whole series of 101 sheets was withdrawn in 1980, but remains a useful source of collected information on basic industrial chemicals.
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Plant/Oper. Progress	*Plant Operations Progress* continues as *Process Safety Progress* 1993-
Pot. Incid. Rept.	*ASESB Potential Incident Report*, Washington, Armed Services Explosives Safety Board
Proc. nth Combust. Symp.	*Proceedings of Combustion Symposia*, various Eds. and Publishers, dated year following the event. 1st Symposium 1928; 19th Symposium, 1982
Renfrew, 1981	*Safety in the Chemical Laboratory*, Collected reprinted articles from *J. Chem. Educ.*, Renfrew, M. M. (Ed.), Vol. IV, 1981
Rodd, 1951–62	*The Chemistry of Carbon Compounds*, Rodd, E. H. (Ed.), London, Elsevier, Vol. 1A, 1951, Vol. 5, 1962; 2nd edn. began in 1979
RSC Data Sheets, 1982 to date	*Laboratory Hazard Data Sheet Series*, Cambridge, Royal Society of Chemistry, No. 1, 1982; No. 89, 1989, issued monthly, ceased 1993
RSC Safety Data Sheets, 1989	*Chemical Safety Data Sheets*, Cambridge, Royal Society of Chemistry, 1989 Generally similar to the monthly Laboratory Hazards Safety Data Sheet series, but the information is presented under headings reflecting legislative requirements. Volume 1 deals with some 100 largely organic liquid solvents and reagents, while Volume 2 covers main group metals and their compounds, 122 items in all. Vol. 3; Corrosives and Irritants, 1990. Vol 4; Toxic Chemicals, Pt. I 1990, Pt. II 1991. Vol 5, Flammables, 1989. There is considerable overlap among the volumes
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Weast, 1988	*Handbook of Chemistry and Physics*, Weast, R. C. (Ed.), Boca Raton (Fa.), CRC Press, 1988; continued under the editorship of Lide, D. R.
Whitmore, 1921	*Organic Compounds of Mercury*, Whitmore, F. C., New York, Chemical Catalog Co. Inc., 1921
Yoshida, 1980	*Handbook of Hazardous Reactions with Chemicals*, Yoshida, T., Tokyo, Tokyo Fire Department, 1980 (copy in British Library, Boston Spa)
Zabetakis, 1965	*Flammability Characteristics of Combustible Gases and Vapours*, Zabetakis, M. G., Washington, US Bureau of Mines, 1965

DropBooks

Appendix 2

Glossary of Abbreviations and Technical Terms

Aerobic	In presence of air
AIT	Autoignition temperature
Alloy	Mixture of 2 or more metals
Amalgam	Alloy of a metal with mercury
Ambient	Usual or surrounding
Anaerobic	In absence of air
Analogue	Compound of the same structural type
AO	Active oxygen content of peroxides
Aprotic	Without labile hydrogen atom(s)
Aqua regia	Mixture of nitric and hydrochloric acids
ARC	Accelerating rate calorimetry
ASTM	American Society for Testing and Materials
Autoxidation	Slow reaction with air
BAM	Bundes Anstalt fur Materialsprufung (similar to ASTM)
Basic	Fundamental, or, alkaline (acting as a base)
BLEVE	Boiling liquid expanding vapour explosion
Blowing agent	Material producing much gas on decomposition
b.p.	Boiling point
BSC	Bench scale calorimeter
Carbonaceous	Containing elemental carbon (as opposed to organic, containing combined carbon)
CHETAH	A computer program to predict energy release hazards
CIT	Critical ignition temperature
Class	Collection of related chemical groups or topics
COI	Critical oxygen index
conc.	concentrated
Congener	Compound with related but not identical structure
COT	Cyclooctatetraene
Critical diameter	Minimum diameter of an explosive charge capable of maintaining detonation
Cryogenic	At a very low (freezing) temperature
CVD	Chemical vapour deposition

Deflagration	Self sustaining internal combustion propagating by means of molecular heat transfer slower than the speed of sound (the explosion mechanism gunpowder and other 'low' explosives)
DH°f	Standard heat of formation
Desiccate	Dry intensively
Detonable	Capable of detonation
Detonation	A self sustaining decomposition reaction propagating faster than the speed of sound by means of a shock wave (the characteristic property of 'high' as opposed to 'low' explosives).
Diglyme	Diethyleneglycol dimethyl ether
Digol	Diethyleneglycol
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EL	Explosive limits (or Flammable limits), vol% in air
Endotherm	Absorption of heat
ESCA	Electron scanning chemical analysis
Exotherm.	Liberation of (reaction) heat
Freeze drying	Drying without heat by vacuum evaporation of frozen solvent
GLC	Gas-liquid chromatography
Glyme	Diethyleneglycol monomethyl ether
Halocarbon	Partially or fully halogenated hydrocarbon
HMPA	Hexamethylphosphoramide
HMSO	Her Majesty's Stationery Office
Homologue	Compound of the same (organic) series
Hypergolic	Ignites on contact
Ignition source	A source of energy which ignites flammables
IMS	Industrial methylated spirit (ethanol)
Induction period	Delay in reaction starting, caused by inhibitors
Inorganic	Not containing combined carbon, of mineral origin
Intermolecular	Between different molecules
Intramolecular	Within the same molecule
IR	Infrared spectroscopy
Initiation	Triggering of explosion or decomposition
LAH	Lithium tetrahydroaluminate
Lanthanide	Of the group of rare-earth metals
LRS	Laser Raman spectroscopy
LPG	Liquefied petroleum gas
MAPP	Methylacetylene/propadiene/propene mixture
Molecular sieve	A zeolite lattice with micropores of specific sizes, useful for molecular separations

DropBooks

m.p.	Melting point
MRH	Maximum reaction heat
NMR	Nuclear magnetic resonance spectrosopy
Nomenclature	System of naming chemicals
Off-spec.	Off-specification (low quality)
Oleum	Sulfar trioxide dissolved in sulfuric acid
Organic	A compound containing combined carbon
Organometallic	Containing carbon to metal bonding
Oxidant	Oxidising agent (electron sink)
PCB	Polychlorinated biphenyl
PTFE	Polytetrafluoroethylene
Propagation	Spread or transmission of decomposition, flame or explosion
Propellant	Energetic composition used in ballistics
PVC	Polyvinyl chloride
Pyrophoric	Igniting on contact with air (or frictional sparking)
Q	Heat of (exothermic) reaction or polymerisation
Quaternary salt	Tetra-substituted ammonium salt etc.
RCHD	Reactive Chemical Hazards Database, which you are using
Redox compound	Compound with reducing and oxidising features
Reducant	Reducing agent (electron source)
Refractory	Heat resisting
REITP2	A computer program to calculate MRH
RSC	Reaction Safety Calorimeter, or Royal Society of Chemistry
Runaway	Reaction out of control
Self-accelerating	Reaction catalysed by its own products
Self-heating	When substance generates heat faster than it is dissipated
Silicones	Organic derivatives of a polysiloxane chain
Slurry	Pourable mixture of solid and liquid
Smelt	Molten sodium sulfide and carbonate from evaporated sulfite liquor
Substance	Not a single chemical species, often of natural origin
Superheated	A liquid at a temperature above its boiling point
Tait24	Temperature of adiabatic storage which gives an induction time to exothermic decomposition of 24 hours
Thermite reaction	Reaction of aluminium powder and iron oxide producing molten iron (and analoguous reactions)
THF	Tetrahydroffiran
TGA	Thermogravimetric analysis
Thermochemistry	Study of heat effects of chemical reactions
TLC	Thin layer chromatography
TNT	Trinitrotoluene
U	Heat of (exothermic) decomposition

Unit operation	A single operational stage of a chemical process sequence
Unit process	A single chemical reaction stage in a process sequence
USNTIS	US National Technical Information Service
UV	Ultraviolet spectroscopy

DropBooks